

Practical Handbook of

SOIL, VADOSE ZONE,
and GROUND-WATER
CONTAMINATION

*Assessment, Prevention,
and Remediation*

SECOND EDITION

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J. Russell Boulding • Jon S. Ginn



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Preface to the Second Edition

I would like to think that the popularity of the first edition of this book is a measure of success in meeting the goals I outlined in the preface to the first edition. With this second edition I welcome Jon Ginn as a co-author. Since entering semiretirement in 1997, I have kept abreast of new developments in site characterization technologies through my part-time association with the Applied Geology and Environmental Management Section of the Environmental Research Division at Argonne National Laboratory. Jon's up-to-date expertise in remediation technologies has been essential for updating Part III of this book, and he has made valuable contributions to updating other sections of the book as well. The basic approach and organization of this book remain the same. Since the first edition was published in 1995, many of the advances that have taken place in the assessment and remediation of soil and ground-water contamination have been more refinements of existing techniques in terms of either instrumentation or computer processing. The text of this new edition has been revised throughout to note refinements or new applications of existing methods. Also, more than 600 new references have been indexed and added to the topical major reference lists at the end of each chapter. For those who may be familiar with the first edition, major revisions and new sections are identified below.

Part I (Basic Concepts) is essentially the same except for the following:

- In Chapter 2, Section 2.4.3 on soil moisture retention relationships has been added, and at the end of the chapter information on the U.S. Geological Survey's *Ground Water Atlas of the United States*, current as of 2002, has been added.
- In Chapter 3, Section 3.3.2 (Hydrolysis) and Section 3.5.4 (Biotransformation of Organic Contaminants) have been expanded.
- In Chapter 4, Section 4.5.3 (Retardation by Sorption) and Section 4.6 (Phase Partitioning to Assess Presence of DNAPLs in the Subsurface) have been added.

Part II (Assessment and Monitoring) has a number of new sections and subsections:

- Special Considerations for DNAPL Investigations (Section 5.1.4)
- Accelerated/Expedited Site Characterization Approaches (Section 5.1.5)
- CPT and Other Direct-Push Sensing Methods (Section 6.5)
- Alcohol Tracers (Section 8.3.5)
- Divergent-Line-Drive Techniques (Section 8.5.4)
- New Developments in Multilevel Sampling (Section 9.5.4)
- Neural Networks and Automated Image Processing (Section 10.5.6)

Part III (Prevention and Remediation) also has a number of new sections:

- Passive Soil Vapor Extraction (Section 13.2.5)
- Soil Thermal Extraction Methods (Section 13.4.4)
- Permeable Reactive Treatment Walls (Section 14.6.3)
- Phytoremediation (Section 14.6.4)
- Enhanced Natural Attenuation (Section 14.6.5)

In addition to revisions to Appendix A (Summary Information on Major Subsurface Characterization and Monitoring Techniques) to add a number of new techniques, a new Appendix B provides a comprehensive index and listing of more than 500 American Society for Testing and Material (ASTM) standard guides, practices, and test methods that may be useful in the field or laboratory for environmental site characterization. Appendix C (Tables and Figures for Estimation of Aquifer Parameters) includes several new empirical equations for estimating hydraulic conductivity from grain size and for estimation of hydrodynamic dispersivity. Finally, a new Appendix E has been added which includes simple problems (with solutions at the end) for determining aquifer properties and contaminant fate and transport behavior.

Preface to the First Edition

My goal in writing this book has been to create a single, convenient reference source to be used (1) as a starting point for obtaining answers to questions that any environmental manager or professional might have about contaminated soil or ground-water, or (2) as a textbook for a college course that focuses on technical aspects of soil and ground-water contamination assessment and management.

Environmental professionals, managers, and regulators without specialized training in soils, geology, geomorphology, vadose-zone and ground-water hydrology, soil and ground-water chemistry, and microbiology will find that the four chapters in Part I (Basic Concepts) provide a comprehensive, yet accessible introduction to those topics as they relate to soil and ground water contamination.

Project planning and field personnel involved in investigating contaminated sites will find that the six chapters in Part II (Assessment and Monitoring) provide up-to-date and comprehensive information on methods for characterizing contaminated sites and analyzing site data.

Decision makers, project planners, and other environmental professionals will find that the four chapters in Part III (Prevention and Remediation) provide systematic and practical information for identifying and implementing methods for (1) preventing or minimizing contamination and (2) cleaning up sites that are already contaminated.

NOTE ABOUT REFERENCE CITATIONS IN THIS HANDBOOK

In order to minimize duplication of references in this handbook, references are cited in four ways:

- Major references are grouped into 23 topics, which follow index tables at the end of each chapter. A master list of these index tables and bibliographies can be found at the end of the Table of Contents.
- Citations in the text are given as footnotes, unless they are contained in a reference table, in which case the reference table number is given. For example, Sara (2002/T9.10) indicates that the full citation can be found in Table 9.10.
- Increasingly, government documents are available electronically on the Internet. Internet sites are identified by brackets: < >. For example, one source of EPA documents is <clu-in/techpubs.htm>.
- Sources for figures and tables in Chapters 1 through 14 are given in Appendix F, which also serves as a master list with the page on which figures and tables can be found. Full citations for references cited in Appendices A through D appear at the end of each appendix.
- ASTM standard methods are cited by the ASTM designation number in the text. Full citations for ASTM test methods can be found in Appendix B, which provides a comprehensive index and listing of ASTM standards that may be useful for environmental site characterization.

Where government documents are cited, the place where documents can be obtained is given or, if the document is available from the National Technical Information Service, the NTIS acquisition number is given. U.S. EPA's National Service Center for Environmental Publications (NSCEP) is the best place to contact for obtaining EPA documents (NSCEP, P.O. Box 42419, Cincinnati, OH 45242-0419; 800-490-9198). This book may refer to earlier names for NSCEP: Center for Environmental Research Information (CERI) or National Center for Environmental Publications and Information (NCEPI). If NSCEP does not have the document, it will refer the request to the appropriate EPA office or provide the NTIS acquisition number. Table 5.3 identifies phone numbers for other EPA hotlines and information sources. Documents available from NTIS can be obtained by calling 800-553-6847 or writing to: National Technical Information Service, Springfield, VA 22161.

NOTE ABOUT GROUND WATER HYPHENATION CONVENTIONS

There are few words in the environmental literature that have greater editorial inconsistency than ground water. The preferred ASTM usage of two words for *ground water* (to parallel *surface water*, which is never written as a single word) is used in this handbook, except when reference citations use a single word, *groundwater*, in the title, in which case they are cited as written. Given the inconsistency in hyphenation practices for the terms *vadose zone* and *ground water* in the literature, I have chosen as a matter of personal preference to use the following conventions: (1) *neither* vadose zone nor ground water is hyphenated when it serves as a modifier in chapter, section, figure, and table titles because I think it looks better that way; (2) vadose zone is *not* hyphenated in normal text when it serves as a modifier because that seems to be the most common usage in the vadose zone literature; and (3) ground water *is* hyphenated when it serves as a modifier because that seems to be the more common usage in the ground-water literature. I think it was Ralph Waldo Emerson who said “Foolish consistency is the hobgoblin of little minds.” I have tried to consistently follow the above inconsistent conventions, but am not overly concerned if I have not entirely succeeded.

ABBREVIATIONS AND ACRONYMS

AGWSE	Association of Ground Water Scientists and Engineers (NWWA/NGWA)
API	American Petroleum Institute
CERI	Center for Environmental Research Information (now NSCEP)
CPT	Cone penetration test
DNAPL	Dense nonaqueous phase liquid
EPA	U.S. Environmental Protection Agency
HEW	U.S. Department of Health, Education and Welfare
HMCRI	Hazardous Materials Control Research Institute
IGWMC	International Ground Water Modeling Center
LNAPL	Light nonaqueous phase liquid
NAPL	Nonaqueous phase liquid
NCEPI	National Center for Environmental Publications and Information (now NSCEP)
NSCEP	National Service Center for Environmental Publications (U.S. EPA)
NWWA/NGWA	National Water Well Association (named changed to National Ground Water Association in 1992)
PAH	Polynuclear aromatic hydrocarbon
PNA	Polynuclear aromatic compound
RCRA	Resource Conservation and Recovery Act
WHPA	Wellhead protection area

The Authors

J. Russell Boulding first began working in the environmental field in 1973 when he helped set up the Environmental Defense Fund's Denver Office, and has been a freelance environmental consultant since 1977 when he established Boulding Soil-Water Consulting in Bloomington, Indiana. Boulding Soil-Water Consulting was closed in 1997, but Mr. Boulding continues to work part-time with the Applied Geoscience and Environmental Management Section of the Environmental Research Division of Argonne National Laboratory. He has a B.A. in geology (1970) from Antioch College, Yellow Springs, Ohio, and an M.S. in water resources management (1975) from the University of Wisconsin–Madison. From 1975 to 1977 he was a soil scientist with the Indiana Department of Natural Resources and mapped soils in southern Indiana on a cooperative program with the U.S. Soil Conservation Service. From 1984 to 1997 he held the position of senior environmental scientist with Eastern Research Group, Inc., in Lexington, Massachusetts.

Mr. Boulding is the author of more than 160 books, chapters, articles, and consultant reports in the areas of soil and ground-water contamination assessment, geochemical fate assessment of hazardous wastes, mined land reclamation, and natural resource management and regulatory policy. From 1978 to 1980 he served as a member of the Environmental Subcommittee of the Committee on Surface Mining and Reclamation (COSMAR) of the National Academy of Sciences (NAS) and as a consultant to the NAS Committee on Soil as a Resource in Relation to Surface Mining for Coal. Mr. Boulding is an ARCPACS-certified professional soil classifier.

Since 1992 he has been a member of the American Society for Testing and Materials' Committee D18 (Soil and Rock) and active in Subcommittees D18.01 (Surface and Subsurface Characterization) and D18.21 (Ground Water and Vadose Zone Investigations). From 1993 to 1997 he chaired D18.01's Section on Site Characterization for Environmental Purposes, and he is the principal author of five ASTM standards, including D5730 (*Guide for Site Characterization for Environmental Purposes*), D6235 (*Practice for Expedited Site Characterization of Vadose Zone and Ground Water Contamination at Hazardous Waste Contaminated Sites*), and D6169 (*Guide for Selection of Soil and Rock Sampling Devices for Use with Drill Rigs*). In January 2001 he received the Ivan A. Johnson Outstanding Achievement Award for outstanding and significant contributions to ASTM Committee D18 on Soil and Rock.

Jon S. Ginn began work in the environmental field in 1995 for the Environmental Management Directorate, at Hill Air Force Base (HAFB), Utah. He worked as the program manager for innovative technology demonstrations and provided technical oversight, project management, and regulatory coordination for numerous innovative remedial technology demonstrations. During the 6 years he worked at Hill, he managed over \$17 million in internal and external funded research, including surfactant enhanced aquifer remediation, partitioning interwell tracer tests for DNAPL characterization, thermally enhanced aquifer remediation, air sparging, bioventing of nonpetroleum hydrocarbons, three-dimensional seismic reflection, and enhanced bioremediation studies. He also served for 3 years as the HAFB regulatory compliance protocol manager for petroleum, oils, and lubricants (POL) under the Environmental Compliance Assessment and Management Program (ECAMP) at Hill Air Force Base.

In 2001, Dr. Ginn joined Select Engineering Services, Inc., Ogden, Utah. He provides technical oversight and program management for the Tactical Shelter and Radome Program office at Hill Air Force Base. Specific projects include the development and integration of composite technology for tactical shelters, radomes, and towers. He also provides technical oversight and program support for the Pollution Prevention Program Office at Hill Air Force Base regarding alternative energy, compliance site inventory, and process-specific opportunity assessments. He received his B.S. in civil engineering from Texas A&M University in 1987 and an M.S. in civil engineering from Texas A&M University in 1990. In 1997, he received his Ph.D. from Utah State University in environmental engineering.

Acknowledgments

This book represents the synthesis and, in a sense, the culmination of work done from 1989 to 1995 on a series of technology transfer documents written wholly or in part by the author for U.S. EPA's Center for Environmental Research Information. At the project management level, Heidi Schultz (Eastern Research Group) and Carol Grove and Sue Schock (U.S. EPA/CERI) require special recognition.

The starting point for this book was a 700-page manuscript that was an expanded and extensively revised version of EPA's 1987 *Ground Water Handbook* (EPA/625/6-87/016), which was written by Michael Barcelona, Joseph Keely, Wayne Pettyjohn, and Allen Wehrmann. Chapter 7 of that document drew heavily upon another EPA report, *Introduction to Ground Water Tracers* (EPA/600/2-85/022), by S.N. Davis, D.J. Campbell, H.W. Bentley, and T.J. Flynn, and Chapter 8 on Joseph Keely's monograph *The Use of Models in Managing Ground-Water Protection Programs* (EPA/600/8-87/003). As it turned out, the author's revised versions of Chapters 7 and 8 are the only ones that were published in EPA's second edition of the *Ground Water Handbook, Volume I: Ground Water and Contamination* (EPA/625/6-90-16a) and *Volume II: Methodology* (EPA/625/6-90-16a), both of which are available from the Center for Environmental Research Information. These, with third-generation revisions and updating, appear in this handbook as Chapter 8 (Soil and Ground Water Tracers) and Chapter 10 (Use of Models and Computers in Contaminant Investigations). To the extent that material originally written by the above-mentioned individuals can be found in this handbook, they deserve credit. Maureen Casey and Leslie Sparrow, HydroQual, Inc., New Jersey, made significant contributions to chapters on monitoring well design and construction, ground-water sampling, and ground-water restoration in the manuscript mentioned at the beginning of this paragraph, some of which has probably made its way into this handbook.

Other individuals who require special recognition for textual contributions to this handbook are Ron Sims and Judy Sims, whose chapters in EPA's *Site Characterization for Subsurface Remediation* on basic approaches to soil and ground-water remediation and on remediation techniques for contaminated soils formed the starting point for Chapters 12 and 13 in this handbook. I was technical editor of that document, and co-author with Michael Barcelona of chapters on basic statistical and analytical concepts and geochemical sampling of subsurface solids and ground-water, which provided the basis for much of Chapter 5 of this handbook.

Anyone bothering to read these acknowledgments may wonder if I can take credit for any of the contents of this handbook. I am the original author of Chapter 3 (Soil and Ground Water Geochemistry and Biology), Chapter 4 (Sources and Behavior of Subsurface Contaminants), Chapter 6 (Geophysical and Remote Sensing Techniques), Chapter 11 (Prevention and Minimization of Contamination), all reference tables and compilations, and all the appendices. All other chapters represent second- to fourth-generation edits, revisions, or updates on my part.

In various incarnations, the material in this handbook has benefited from the technical review and suggestions from many individuals: Gina Bochicchio, Fred Cornell, Larry Eccles, Lorne Everett, Malcolm Field, Pete Haeni, Paul Heigold, Jan Hendrickx, Beverly Herzog, Dave Kaminski, Jack Keeton, Scott Keys, Eric Koglin, Duncan McNeill, Gary Olhoeft, Robert Powell, Robert Puls, Charlie Riggs, Ron Schalla, Ron Sims, Jim Ursic, Paul van der Heijde, Mark Vendl, and John Williams. Special thanks are due to my colleagues on ASTM's Environmental Site Characterization Task Group (Joe Downey, Ed Gutentag, and Mario Fernandez) and to Gareth Davies and Mark Kram for review of individual or multiple chapters. Special thanks also to Cathy Wootton Clayton for her work on graphics and image production.

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PART I

Basic Concepts

Geology, Soils, and Geomorphology

Geology, the study of the earth, includes the investigation of earth materials, the processes that act on these materials, the products that are formed, the history of the earth, and the origin and development of life-forms. There are several subfields of geology. *Physical geology* deals with all aspects of the earth and includes most earth science specialties. *Historical geology* is the study of the origin of the earth, continents and ocean basins, and life-forms. *Economic geology* is an applied approach focusing on the search and exploitation of mineral resources, such as metallic ores, fuels, and water. *Structural geology* deals with the various structures of the earth and the forces that produce them. *Geophysics* is the examination of the physical properties of the earth and includes the study of earthquakes and methods to evaluate the subsurface.

All of the geology subfields are used to some extent in the study of ground water. Probably the most difficult concept to comprehend by individuals with little or no geological training is the complexity of the subsurface, which is hidden from view and, at least presently, cannot be adequately sampled. A guiding principle in geologic and hydrogeologic studies is that the present is the key to the past. The processes occurring today are the same processes that have occurred throughout geologic history, although their magnitude may vary with time. Furthermore, an understanding of present processes, and how they have acted in the past, can be used as a guide to predict the future.

Soil science, also called *pedology*, and *geomorphology*, the study of surface landforms, are disciplines related to geology but focusing on the earth's surface. Geology, soil science, and geomorphology are intimately related and concerned with many of the same earth processes, such as weathering, erosion, and deposition. Nevertheless, each of these disciplines has a distinct perspective that is usually helpful and often essential in the study of ground-water contamination.

This chapter provides a brief description of fundamental concepts in geology, soil science, and geomorphology as they relate to ground-water contamination. Sections 1.1 (Geologic Materials), 1.2 (Geologic Processes), and 1.3 (Stratigraphy and Structure) focus on geology. Section 1.4 examines basic soil concepts and Section 1.5 geomorphic concepts, with special emphasis on karst geomorphic settings because of their distinctive hydrogeologic characteristics, which include very rapid movement of contaminants in the subsurface.

1.1 GEOLOGIC MATERIALS

Geologic materials result from constant changes at the earth's surface and subsurface. Over long periods of time these changes affect the location, quality, and movement of ground water. Rocks that rise as mountains over millions of years will be gradually eroded and transported by wind, water, or gravity to low-lying areas. Variations in these transport processes alter particles

physically and chemically, giving rise to deposits of unique texture and composition. Grain-size variations and degree of sorting will cause differences in permeability and ground-water velocity, while changes in mineral composition can lead to variations in water quality.

1.1.1 Mineralogy

Minerals are the basic building blocks of rocks. Most minerals contain two or more elements, but of all the elements known, only eight account for nearly 98% of the rocks and minerals:

Oxygen	46%
Silicon	27.7%
Aluminum	8.1%
Iron	5.0%
Calcium	3.6%
Sodium	2.8%
Potassium	2.6%
Magnesium	2.1%

A general understanding of mineralogy is important to the study of ground water because it is the mineral composition of rocks that, to a large extent, controls the quality of water that a rock contains under natural conditions and the chemical reactions between rock and contaminants or naturally occurring substances.

The most common rock-forming minerals can be divided into four broad groups: (1) oxides, carbonates, and sulfates; (2) silicates; (3) clay minerals; and (4) common ores. Organic matter, from which oil shales, coal, and petroleum deposits form, is another important material that is discussed in Section 3.4.4 because of its geochemical importance in soil and ground-water chemistry.

Oxides, Carbonates, and Sulfates. *Quartz* (SiO_2), one of the most common minerals, is hard and resistant to both chemical and mechanical weathering. In sedimentary rocks, quartz occurs as sand-size grains (sandstone) or finer silt- and clay-size grains. It may also appear as a silica cement. Because of the low solubility of silica, it generally appears in ground water in concentrations of less than 25 mg/l.

Limonite is actually a group name for the hydrated ferric oxide minerals ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) that occur so commonly in many types of rocks. Limonite is generally rusty or blackish with a dull, earthy luster. It is a common weathering product of other iron minerals. Because limonite and other iron-bearing minerals are nearly universal, dissolved iron is a very common constituent in water, causing staining of clothing and plumbing fixtures.

The major carbonate minerals are *calcite* (CaCO_3), the major component of limestone, and *dolomite* ($\text{CaMg}(\text{CO}_3)_2$). Dolomite is also the name of carbonate sediments enriched with this magnesium carbonate. *Gypsum*, a hydrated calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), occurs as a sedimentary evaporite deposit and as crystals in shale and some clay deposits. Quite soluble, it is the major source of sulfate in ground water.

Silicates. The most common rock-forming silicate minerals include the feldspars, micas, pyroxenes, amphiboles, and olivine. Feldspars, the most abundant minerals on earth, are aluminosilicates of potassium or sodium and calcium. Most of the minerals in this group are white, gray, or pink. Upon weathering, they turn to clay and release the remaining chemical elements to water. Muscovite and biotite mica are platy aluminosilicate minerals that are common and easily recognized in igneous, metamorphic, and sedimentary rocks. Pyroxenes, a group of silicates of calcium, magnesium, and iron, as well as amphiboles, which are complex hydrated silicates of calcium, magnesium, iron, and aluminum, are common in most igneous and metamorphic rocks. They appear as small, dark crystals. Olivine, a magnesium-iron silicate, is generally green or yellow and is common in certain igneous and metamorphic rocks. None of the rock-forming silicate minerals has a major impact on water quality in most situations.

Clay Minerals. Next to organic matter (see Section 3.4.4), clay minerals are the most chemically active materials in soil and unconsolidated geologic materials. Both consolidated materials composed of clay minerals (shales) and clayey unconsolidated materials tend to have low permeabilities, and consequently, water movement is very slow. Because of their geochemical significance in the study of ground-water contamination, clay minerals are described in more detail here than the other major mineral groups. Two broad groups of clay minerals are recognized: silicate clays and hydrous oxide clays.

Silicate clays form from the weathering of primary silicate minerals such as feldspars and olivine. They have a sheet-like lattice structure with either silicon (Si) in coordination with four oxygen atoms (silica tetrahedra) or aluminum (Al) in coordination with six oxygen atoms (alumina octahedra). The strong sorptive capacity of clay derives from the negative charges created at the edges of these crystalline sheets where oxygen atoms (O^{2-}) have extra electrons that are not bonded to the cations in the crystalline structure. The negative charge can be further increased when ions with a lower valence substitute for ions with a higher valence in the sheet structure (for example, Al^{+3} substitutes for Si^{+4} in tetrahedral sheets, and Mg^{+2} substitutes for Al^{+3} in octahedral sheets).

Silicate clays are classified according to different stacking arrangements of the tetrahedral (silica) and octahedral (alumina) lattice layers and their tendency to expand in water. The stacking type strongly affects certain properties of clays, including (1) surface area, (2) the tendency to swell during hydration, and (3) *cation exchange capacity* (CEC), which is a quantitative measure of the ability of a mineral surface to adsorb ions. CEC is the sum of exchangeable cations that a material can adsorb at a specific pH. Standard International (SI) units for CEC are centimoles per kilogram, but it is also commonly reported as milliequivalents (meq) per 100 g, where 1 meq is defined as 1 mg of hydrogen or the amount of any other ion that will combine with or displace 1 mg of hydrogen. These units are interchangeable ($1 \text{ cmol/kg} = 1 \text{ meq/100 g}$).

Table 1.1 summarizes some properties of different silicate clay minerals. The montmorillonite group of silicate clays is most sensitive to swelling and has a high CEC. This type of clay has these characteristics because the 2:1 lattice structure (two octahedral sheets separated by a tetrahedral sheet) forms sheets that are loosely connected by exchangeable cations. The exchange sites between 2:1 lattice layers can be easily hydrated (i.e., adsorb water molecules) under certain

Table 1.1 Important Characteristics of Silicate Clay Minerals

Property	Type of Clay ^a				
	Montmorillonite (Smectite) ^b	Vermiculite	Illite	Chlorite	Kaolinite
Lattice type ^c	2:1	2:1	2:1	2:2	1:1
Expanding?	Yes	Slightly	No	No	No
Specific surface area (m ² /g)	700–800	700–800	65–120	25–40	7–30
External surface area	High	High	Medium	Medium	Low
Internal surface area	Very high	High	Medium	Medium	None
Swelling capacity	High	Medium-high	Medium	Low	Low
Cation exchange capacity (meq/100 g)	80–150	100–150+	10–40 ^e	10–40 ^e	3–15 ^e
Other similar clays	Beidellite				Halloysite
	Nontronite				Anauxite
	Saponite				Dickite
	Bentonite ^d				Nacrite

^a Clays are arranged from most reactive (montmorillonite) to least reactive (kaolinite).

^b The term *smectite* is now used to refer to the montmorillonite group of clays (Soil Science Society of America, 1987/T1.3).

^c Tetrahedral:octahedral layers.

^d Bentonite is a clay formed from weathering of volcanic ash and is made up mostly of montmorillonite and beidellite.

^e Upper range occurs with smaller particle size.

Source: Boulding (1990).

conditions. Because the water molecules have a greater diameter than the cations that hold the sheets together, hydration pushes the layers farther apart. Vermiculite has stronger negative charges on its inner surfaces than montmorillonite because of the substitution of lower-valence magnesium ions for aluminum. This factor results in an even higher CEC than that found in montmorillonite, but it also has the effect of bonding the 2:1 sheets more strongly. Consequently, vermiculite clays are less susceptible to swelling.

In [Table 1.1](#), the clays are listed in sequence from most reactive (montmorillonite and vermiculite) to least reactive (kaolinite). The 1:1 lattice structure in kaolinite creates strong bonds between the paired sheets, resulting in a low surface area and CEC. Illite and chlorite have intermediate surface areas, CEC, and sensitivities to swelling.

Clay minerals in sedimentary formations are usually mixtures of different groups. In addition, *mixed-layer* clay minerals can form. These minerals have properties and compositions that are intermediate between two well-defined clay types (i.e., chlorite-illite, illite-montmorillonite, etc.). Where soils have a high clay content, clay mineralogy is a criterion for classification of soils in the U.S. Department of Agriculture (USDA) soil taxonomy ([Section 1.4.2](#)). Such soils are identified by the dominant clay (halloysite, illite, kaolinite, montmorillonite, etc.) or as having mixed mineralogy.

Hydrous oxide clays are less well understood than silicate clays. These clays are oxides of iron, magnesium, and aluminum that are associated with water molecules, although the exact mechanism by which the water molecules are held together is somewhat uncertain. Because of the lower overall valence of the cations in hydrous oxide clays compared to silicate clays, CEC is lower in hydrous oxide clays. However, hydrous oxides of magnesium (Mn) and iron (Fe) can furnish the principal control on the fixation of cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn) heavy metals in soils and freshwater sediments.¹

Ores. The three most common ore minerals are galena, sphalerite, and pyrite. Galena, a lead sulfide (PbS), is heavy, brittle, and breaks into cubes. Sphalerite is a zinc sulfide (ZnS) mineral that is brownish, yellowish, or black. It ordinarily occurs with galena and is a major zinc ore. The iron sulfide pyrite (FeS), which is also called fool's gold, is common in all types of rocks. Weathering of this mineral leads to acid-mine drainage, a major surface and ground-water quality problem in certain coal mining areas of the Midwest and Appalachia and in metal sulfide mining regions.

1.1.2 Texture and Fabric

The term *texture* has different meanings in geology and soil science. In soil science it is simply the relative proportions of clay-, silt-, and sand-size particles in soil or unconsolidated material. In geology, describing the texture involves characterization of grain size, but also grain shape, degree of crystallization, and contact relationships of grains. The term *fabric* applies to the total of all physical features of a rock or soil that can be observed macroscopically and microscopically. In solid rock this includes texture, porosity, orientation of mineral grains, cleavage, joints, and fractures, all of which may influence water-transmitting characteristics. Soil fabric analysis involves the study of the distinctive physical features resulting from soil-forming processes, which also strongly influence the location and rate of water movement in soil.

A variety of scales are available for the classification of unconsolidated materials based on particle-size distribution. In geology, the *Wentworth–Udden* scale is most widely used: boulder (>256 mm), cobble (64–256 mm), pebble (4–64 mm), granule or gravel (2–4 mm), sand (1/16–2 mm), silt (1/256–1/16 mm), and clay (<1/256 mm). The USDA soil textural classification system is most widely used by soil scientists; engineers usually use the American Society for Testing and Materials (ASTM) version (ASTM D2488/TA.14) of the Unified Soil Classification System (USCS), and less commonly the American Association of State Highway Officials (AASHTO) soil

¹ Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn Concentrations in Soils and Water: The Significant Role of Hydrous Mn and Fe Oxides. In: Adsorption from Aqueous Solution, ACS Advances in Chemistry Series 79, pp. 337–387, American Chemical Society, Washington, D.C.

American Society for Testing and Materials	Colloids *		Clay	Silt			Fine sand		Medium sand		Coarse sand	Gravel			
American Association of State Highway Officials	Colloids *		Clay	Silt			Fine sand		Coarse sand		Fine gravel		Medium gravel	Coarse gravel	Boulders
U.S. Department of Agriculture	Clay			Silt			Very fine sand	Fine sand	Med- ium sand	Coarse sand	Very coarse sand	Fine gravel			Cobbles
Federal Aviation Administration	Clay			Silt			Fine sand		Coarse sand		Gravel				
Corps of Engineers, Bureau of Reclamation	Fines (silt or clay)**						Fine sand		Medium sand		Coarse sand	Fine gravel		Coarse gravel	Cobbles
Sieve sizes															
Particle size.															
.001 .002 .003 .004 .006 .008 .01 .02 .03 .04 .06 .08 .1 2 3 4 .6 .8 1.0 2.0 3.0 4.0 6.0 8.0 10 20 30 40 60 80															

*Colloids included in clay fraction test reports.
**The LL and PI of "Silt" plot below the "A" line on the plasticity chart, Table 4,
and the LL and PI for "Clay" plot above the "A" line.

Figure 1.1 Particle-size limits of different U.S. textural classification systems (Mercer and Spalding, 1991b, after Portland Cement Association, 1973).

classification system. Figure 1.1 compares the grain-size limits for the ASTM, AASTHO, USDA, Federal Aviation Administration (FAA), and the U.S. Army Corps of Engineers/Bureau of Reclamation. Figure 1.2 shows the 12 USDA soil texture classes based on relative percentages of silt, sand, and clay. The hydrologic properties of soils are strongly related to particle-size distribution, and the USDA system is a useful system for estimating a number of these properties (see, for example, Figures C.2, C.8, and C.9).

For several reasons, the term *clay* may be confusing. First, the various particle-size distribution schemes define clay differently. The Wentworth–Udden scale for clay (<0.0039 mm) lies between the AASTHO (<0.005) and the USDA (<0.002) definitions. The ASTM and FAA systems define clay as <0.004 mm, which includes silt-size particles in the USDA system (see Figure 1.1). Second, clay minerals are usually clay-size particles, but may be silt-size. Similarly, nonclay minerals may be clay particles if they are small enough.

1.1.3 Rocks

Three major types of rock make up the earth. *Igneous rocks* have solidified from molten material either within the earth (intrusive) or on or near the surface (extrusive). *Metamorphic rocks* originally were igneous or sedimentary rocks that have subsequently been modified by temperature, pressure, or chemically active fluids. *Sedimentary rocks* result from the weathering of preexisting rocks, erosion, and deposition. While geologists have developed elaborate systems of nomenclature and classification of rocks, only basic rock descriptions having the most value in hydrogeologic studies will be presented here.

Igneous Rocks. Igneous rocks are classified on the basis of their composition and grain size. *Basic* igneous rocks consist mostly of feldspar and a variety of dark, iron- and magnesium-rich minerals (olivine, pyroxenes, and hornblendes). *Acidic* igneous rocks are lighter in color, with feldspar, quartz, and micas being the dominant minerals. If the parent molten material cools slowly deep below the surface, minerals will have an opportunity to grow and the rock will be coarse grained (*gabbro*, if cooled from basic magma, and *granites*, if cooled from acidic magma). Magma

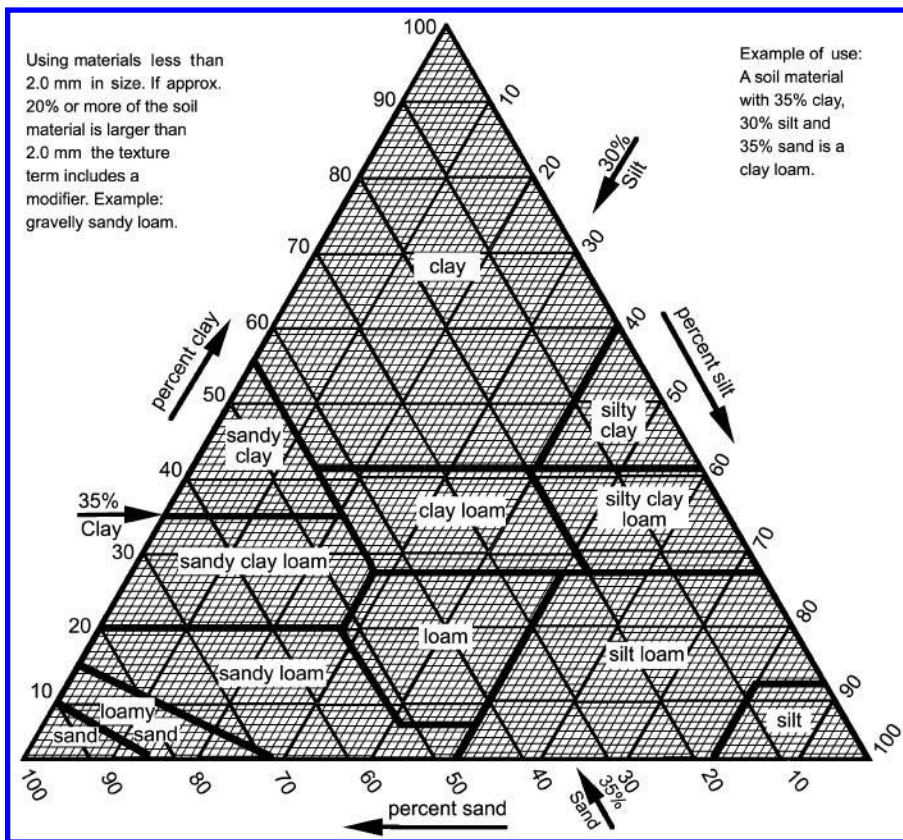


Figure 1.2 Guide for USDA soil textural classification (SCS, 1971).

that cools rapidly, such as that derived from volcanic activity, is so fine grained that individual minerals generally cannot be seen even with a hand lens. *Basalt* is the fine-grained equivalent of gabbro, and *andesite* is the fine-grained equivalent of granite. In some cases, the molten material initially cools slowly, allowing large mineral crystals to grow. If the cooling rate increases, rapid cooling crystallizes the remaining melt into a fine-grained matrix. This texture, consisting of large crystals in a fine-grained matrix, is called *porphyritic*.

Intrusive igneous rocks can only be seen where they have been exposed by erosion. They are *concordant* if they generally parallel the bedding of the enclosing rocks and *discordant* if they cut across the bedding. The largest discordant igneous masses are called batholiths and occur in the eroded centers of many ancient mountains. Their dimensions are in the range of tens of miles. Batholiths usually consist largely of granite, which is surrounded by metamorphic rocks. Other discordant igneous rocks include *dikes* ranging in thickness from a few inches to thousands of feet. Many are several miles long. *Sills* are concordant bodies that have invaded sedimentary rocks along bedding planes. They are relatively thin. Both sills and dikes, when intruded into existing rocks, tend to cool quite rapidly and are fine grained. *Pegmatite* dikes, on the other hand, form in the last stages of a magma's cooling, and can form centimeter- to meter-length crystals.

Extrusive rocks include lava flows or other types associated with volcanic activity, such as the consolidated ash called *tuff*. These are fine grained or even glassy. Some extrusive rocks, like pumice, have sufficiently high porosity resulting from gas bubbles in the magma during cooling that they can float on water.

Igneous rocks are typically dense and have very low porosity and permeability. Most, however, are fractured to some degree and can store and transmit a modest amount of water. These fractures

form preferential flow paths for contaminants, resulting in relatively rapid movement, even though the overall hydraulic conductivity is low. Some lava flows are notable exceptions because they contain large-diameter tubes or a permeable zone at the top of the flow where gas bubbles migrated to the surface before the rock solidified. These rocks are called scoria.

Metamorphic Rocks. Metamorphism is a process that changes preexisting rocks into new forms because of increases in temperature, pressure, and chemically active fluids. Metamorphism may affect igneous, sedimentary, or other metamorphic rocks. The changes brought about include the formation of new minerals, increase in grain size, and modification of rock structure or texture, all of which depend on the original rock's composition and the intensity of the metamorphism.

Some of the most obvious changes are in texture, which serves as a means of classifying metamorphic rocks into two broad groups: foliated and nonfoliated rocks. *Foliated* metamorphic rocks typify regions that have undergone severe deformation, such as mountain ranges. Shale, which consists mainly of silt and clay, is transformed into slate by the change of clay to mica. Mica, a platy mineral, grows with its long axis perpendicular to the principle direction of stress, forming a preferred orientation. This orientation, as in the development of cleavage in slate, may differ greatly from the original bedding.

With increasing degrees of metamorphism, the grains of mica grow larger so that the rock has a distinct foliation texture, characteristic of the metamorphic rock *schist*. At even higher grades of metamorphism, the mica may be transformed to a much coarser grained feldspar, producing the strongly banded texture of *gneiss*.

Nonfoliated rocks include the hornfels and another group formed from rocks that consist mainly of a single mineral. The *hornfels* occur around an intrusive body and were changed by "baking" during intrusion. The second group includes marble and quartzite, as well as several other forms. *Marble* is metamorphosed limestone, and *quartzite* is metamorphosed quartz sandstone.

There are many different types of metamorphic rocks, but from a hydrogeologic viewpoint, they neither store nor transmit much water and are of only minor importance as aquifers. Their primary permeability is notably small, if it exists at all, and fluids are forced to migrate through secondary openings, such as faults, joints, or other types of fractures. As with igneous rocks, the concentration of flow in fractures means that contaminants may move relatively rapidly, especially in response to ground-water pumping.

Sedimentary Rocks. Sedimentary rocks are deposited either in a body of water or on the land by running water, wind, and glaciers. Sediments are first derived by the weathering and erosion of preexisting rocks, and each depositional agent leaves a characteristic stamp on the material it deposits (Section 1.2.3). The change from a loose, unconsolidated sediment to a rock is the process of *lithification*. Unconsolidated sediments are discussed in Section 1.1.4. The most common sedimentary rocks are shale, siltstone, sandstone, and limestone. Although sedimentary rocks appear to be the dominant type, in reality they make up but a small percentage of the earth. They are most readily evident, however, because they form a thin crust over much of the earth's surface. Sedimentary rocks and the unconsolidated materials that serve as precursors to sedimentary rocks are the primary sources of ground water.

Most sedimentary rocks are deposited in a sequence of layers or strata. Each layer or stratum is separated by a bedding plane, which reflects variations in sediment supply or short-term erosion. Bedding planes commonly represent changes in grain size. *Stratigraphic correlation* is the process of matching strata between wells or outcrops (Section 1.3).

Sedimentary rocks are classified on the basis of texture (grain size and shape) and composition. *Clastic* rocks consist of particles of broken or worn material and include shale, siltstone, sandstone, and conglomerate. These rocks were lithified by compaction, in the case of shale, and by cementation. The most common cements are clay, calcite, quartz, and limonite. The last three, carried by ground water, precipitate in the unconsolidated material under specific geochemical conditions.

The *organic* or *chemical* sedimentary rocks consist of strata formed from or by organisms and by chemical precipitates from seawater or other solutions. Most have a crystalline texture. Some

consist of well-preserved organic remains, such as reef deposits and coal seams. Chemical sediments include limestones, dolomites, and evaporites such as halite (sodium chloride), gypsum, and anhydrite (anhydrous calcium sulfate).

The major features of marine sedimentary rocks are their widespread occurrence and generally uniform thickness and composition. If not disturbed by some type of earth movement, they are stratified and horizontal. Furthermore, each lithologic type is unique relative to adjacent units. The bedding planes or contacts that divide them represent distinct differences in texture or composition. From a hydrologic perspective, differences in texture from one rock type to another produce boundaries that strongly influence ground-water flow. Ground water tends to flow parallel to these boundaries, that is, within particular geologic formations rather than across them.

1.1.4 Unconsolidated Materials

Unconsolidated materials may result from the *in situ* weathering of rock or, more commonly, from erosion of weathered material with subsequent deposition at another location. The major characteristics of unconsolidated material are *sorting*, *rounding*, and *stratification*. A sediment is well sorted if the grains are nearly all the same size. Wind is the most effective sorting agent, followed by water. Glacial till is unsorted and consists of a wide mixture of material that ranges from large boulders to clay. [Section 1.2.3](#) describes further the characteristics of waterborne, windborne, and glacial deposits.

While being transported, sedimentary material loses its sharp, angular configuration and develops some degree of rounding. The amount of rounding depends on the original shape, composition, transporting medium, and distance traveled.

Sorting and rounding are important features of both consolidated and unconsolidated material because they are key to controlling permeability and porosity. The greater the degree of sorting and rounding, the higher will be the water-transmitting and storage properties (see Table 7.2). This is why a sand deposit, in contrast to glacial till, can be such a productive aquifer.

1.2 GEOLOGIC PROCESSES

Generally speaking, a rock is stable only in the environment in which it was formed. Once removed from that environment, it begins to change, rapidly in some cases, but more often slowly, by weathering. The two major processes of weathering are mechanical and chemical, and they usually proceed in concert.

1.2.1 Mechanical Weathering

Mechanical weathering is the physical breakdown of rocks and minerals. Fracturing results when water in a crack turns to ice, or from thermal expansion and contraction resulting from daily and seasonal temperature fluctuations. Abrasion occurs during transport by water, ice, or wind. Gravity causes rocks to fall and shatter. Weathering detritus ranges in size from boulders to silt. Mechanical weathering alone only reduces the size of the rock; its chemical composition does not change. Quartz, for example, is very resistant to chemical weathering. However, it does mechanically weather to quartz sand.

1.2.2 Chemical Weathering

Chemical weathering is an actual change in composition as minerals are modified from one type to another. Many, if not most, of the changes are accompanied by a volumetric increase or decrease, which in itself further promotes additional chemical weathering. The rate depends on

temperature, surface area, and available water. The major reactions that occur during chemical weathering are oxidation, hydrolysis, and carbonation. *Oxidation* is a reaction with oxygen (air) to form an oxide, *hydrolysis* is a reaction with water, and *carbonation* is a reaction with CO₂ to form a carbonate. Section 3.3 discusses these chemical processes further. Some of the feldspars weather to clay and release calcium, sodium, silica, and many other elements that are transported in water. The iron-bearing minerals leach iron and magnesium weathering products.

1.2.3 Erosion and Deposition

Once a rock begins to weather, material is transported or eroded and deposited. The major agents involved in this part of the rock cycle are running water, wind, and glacial ice.

Waterborne Deposits. Sediment reaching a stream by gravity or surface erosion is carried to a temporary or permanent site of deposition. During transportation some sorting occurs and the finer silt and clay are carried farther downstream. The streams, constantly filling, eroding, and widening their channels, deposit material that provides clues to much of the history of the region. Alluvial deposits are distinct but highly variable in grain size, composition, and thickness. Where they consist of glacially derived sand and gravel, called *outwash*, they form some of the most productive water-bearing units in the world.

Windborne Deposits. Wind-laid or *eolian* deposits are relatively rare in the geologic record. The massively cross-bedded sandstone of the Navajo Sandstone in Utah's Zion National Park and surrounding areas is a classic example in the U.S. Other deposits are more or less local and are represented by dunes formed along beaches of large water bodies or streams. Their major characteristic is the high degree of sorting. Dunes, being relatively free of silt and clay, are very permeable and porous, unless the openings have been filled by cement. They allow rapid infiltration of water and, if the topographic and geologic conditions are such that the water does not rapidly drain, can form major water-bearing units.

Another wind-deposited sediment is *loess*, which consists largely of silt- and clay-size particles. It lacks bedding but is typified by vertical jointing. Silt is transported by wind from deserts, flood plains, and glacial deposits. Loess weathers to a fertile soil and is very porous. It is common along the major rivers in the glaciated parts of the U.S. and in China, parts of Europe, and adjacent to deserts and deposits of glacial outwash.

Glacial Deposits. Glaciers erode, transport, and deposit sediments that range from clay to huge boulders. They rework the land surface over which they flow and bury former river systems. The areas covered by glaciers during the last Ice Age in the U.S. are shown in [Figure 1.3](#), but the deposits extend far beyond the former margins of the ice. The two major types of glaciers include valley or mountain glaciers and the far more extensive continental glaciers. The deposits they leave are similar, differing for the most part only in scale.

As a glacier passes slowly over the land surface, it incorporates material from the underlying rocks into the ice mass. This material is transported and deposited elsewhere when the ice melts. During this process, glaciers modify the land surface, both through erosion and deposition. The debris associated with glacial activity is collectively termed *glacial drift*. Unstratified drift, usually deposited directly by the ice, is *glacial till*, a heterogeneous mixture of boulders, gravel, sand, silt, and clay. Till often has low porosity due to the extreme pressure exerted on it by the glacial overburden, with ground-water flow concentrated in fractures, as with igneous rocks ([Section 1.1.3](#)). Glacial debris reworked by streams and in lakes is stratified drift. Stream-laid deposits are called *glacial outwash*. Although stratified drift may range widely in grain size, the sorting far surpasses that of glacial till. Glacial lake or *lacustrine* clays are particularly well sorted.

Glacial geologists usually map on the basis of landforms resulting from glacial action, such as moraines, outwash, drumlins, etc. The various kinds of moraines and associated landforms are composed largely of unstratified drift with incorporated layers of sand and gravel. Stratified drift is found along existing or former stream valleys or lakes that were either in the glacier or extended

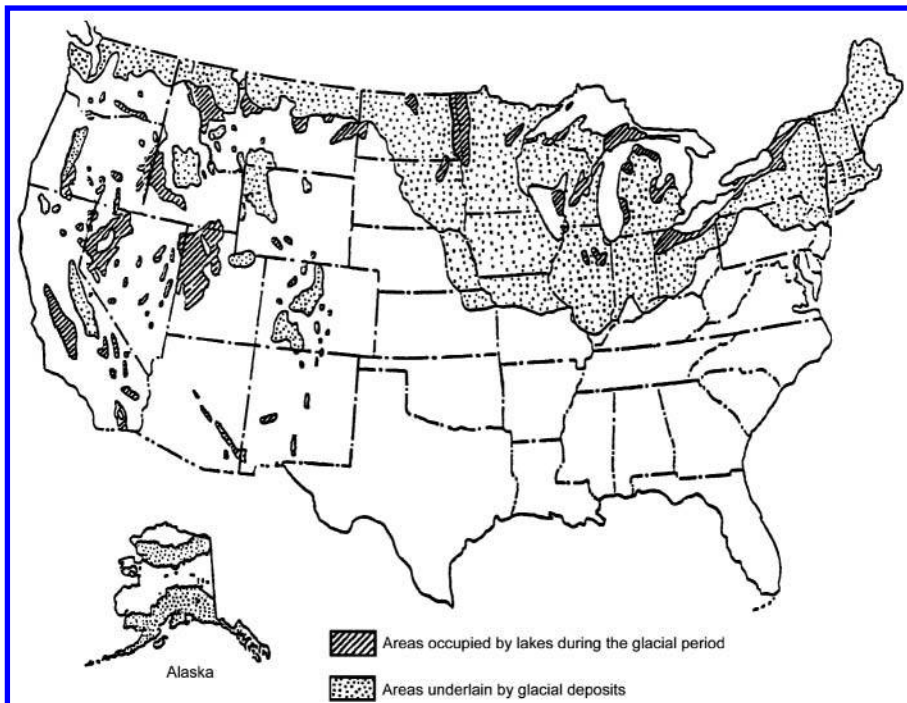


Figure 1.3 Areal extent of glacial deposits in the U.S. (Heath, 1984).

downgradient from it. Meltwater stream deposits are mixtures of sand and gravel. In some places, they have coalesced into extensive outwash plains.

Glaciers advanced and retreated many times, reworking, overriding, and incorporating sediments from previous advances into the ice, subsequently redepositing them elsewhere. There was a constant inversion of topography as buried ice melted, causing adjacent, waterlogged till to slump into the low areas. During advances, the ice might have overridden older outwash layers so that upon melting, these sand and gravel deposits were covered by a younger layer of till. Regardless of the cause, the final effect is a complex history and stratigraphy. When working with glacial till deposits, it is nearly always impossible to predict the lateral extent or thickness of a particular lithology in the subsurface. Surficial stratified drift is more uniform than till in thickness, extent, and texture.

1.3 STRATIGRAPHY AND STRUCTURE

Stratigraphy and structural geology strongly influence the occurrence and behavior of ground water, although structural geology is less important where sediments are flat lying and undisturbed by folding or faulting.

1.3.1 Stratigraphic Relationships

A general principle of geology is that the youngest unit is on the top in any sequence of sedimentary rocks that has not been disturbed by folding or faulting. A second general principle is that sedimentary rocks are deposited in a horizontal or nearly horizontal position. The fact that rocks are found overturned, displaced vertically or laterally, and squeezed into open or tight folds clearly indicates that the earth's crust is a dynamic system.

An *unconformity* is a break in the geologic record. It is caused by a cessation in deposition that is followed by erosion and subsequent deposition. When periods of erosion are protracted and over large geographic areas, significant portions of the geologic record can be destroyed.

If a sequence of strata is horizontal but the contact between two rock groups in the sequence represents an erosional surface, that surface is said to be a *disconformity*. Where a sequence of strata has been tilted and eroded and then younger, horizontal rocks are deposited over it, the contact is an *angular unconformity*. A *nonconformity* occurs where eroded igneous or metamorphic rocks are overlain by sedimentary rocks. A *paraconformity* exists where underlying horizontal sedimentary layers have been eroded and then covered by sediments deposited above them. This type of unconformity is difficult to identify because there is no obvious inconsistency in the strata type or orientation.

1.3.2 Age and Relationship of Stratigraphic Units

Dating of rock units deals with the relation between the emplacement or disturbance of rocks and time. The geologic timescale was developed to provide a standard classification system (Table 1.2) and is based on a sequence of rocks that were deposited during a particular time interval. The divisions are commonly based on some type of unconformity. In considering geologic time, three types of units are defined: rock units, time-rock units, and time units.

A *rock unit* refers to some particular lithology or type of rock. These may be further divided into geologic formations that are of sufficient size and uniformity to be mapped in the field. The Pierre Shale, for example, is a widespread and, in places, thick geologic formation that extends over much of the Northern Great Plains. Formations can also be divided into smaller units called members. Formations have a geographic name that may be coupled with a term that describes the major rock type. Two or more formations comprise a group.

Time-rock units refer to the rock that was deposited during a certain period of time. These units are divided into system, series, and stage. *Time units* refer to the time during which a sequence of

Table 1.2 Geologic Timescale

Era	Period	Epoch	Millions of Years Ago
Cenozoic	Quaternary	Recent	0–0.01
		Pleistocene	0.01–2
	Tertiary	Pliocene	2–5
		Miocene	5–23
		Oligocene	23–34
		Eocene	34–55
		Paleocene	55–65
Mesozoic	Cretaceous		65–144
	Jurassic		144–206
	Triassic		206–250
Paleozoic	Permian		250–290
	Pennsylvanian		290–314
	Mississippian		314–360
	Devonian		360–409
	Silurian		409–439
	Ordovician		439–500
	Cambrian		500–540
Precambrian			540–4600

Note: Dates have an accuracy range of about $\pm 1\%$, but boundary dates continue to change as dating methods are refined.

Source: Update of U.S. EPA (1987a) as of 2002.

rocks was deposited. The time-rock term *system* has the equivalent time term *period*. That is, during the Cretaceous Period, for example, rocks of the Cretaceous System were deposited, consisting of many groups and formations. Time units are named in such a way that the eras reflect the complexity of life-forms that existed, such as the Mesozoic or “middle life.” System or period nomenclature is largely based on the geographic location in which the rocks were first described, such as Jurassic, which relates to the Jura Mountains of Europe.

The terms used by geologists to describe rocks relative to geologic time are useful for ground-water investigations in providing a general overview of the regional geology of an area. The terms alone have no significance as far as water-bearing properties are concerned.

1.3.3 Folds and Fractures

Folds and fractures are the major types of structural features described by geologists. Structural features are usually mapped using a combination of surface outcrop observations, subsurface geophysical measurements, and borehole observations.

Folds. Rocks folded by compressional forces are common in and adjacent to former or existing mountain ranges. The folds range from a few inches to 50 mi or so across. *Anticlines* are rocks folded upward into an arch; their counterpart, *synclines*, are folded downward like a valley (Figure 1.4). A *monocline* is a flecture in which the rocks are horizontal, or nearly so, on either side of the flecture.

Although many rocks have been folded into various structures, this may not be reflected by the topographic features. As uplift proceeds, erosion removes weathering products from the rising mass and deposits them elsewhere. The final topography is related to the erodibility of the rocks, with resistant strata such as sandstone forming ridges, and the less resistant material such as shale forming valleys. Consequently, the geologic structure of an area may bear little resemblance to its topography.

The structure of an area can be determined from field studies or a geologic map, if one exists. Various types of folds and their dimensions appear as unusual patterns on geologic maps. An anticline, for example, will be depicted as a series of rock units in which the oldest is in the middle, while a syncline is represented by the youngest rock in the center (Figure 1.4). More or less equidimensional anticlines and synclines are termed domes and basins, respectively.

The inclination of the top of a fold is the plunge. Folds may be symmetrical, asymmetrical, overturned, or recumbent in relation to the fold axis. The inclination of the rocks is indicated by

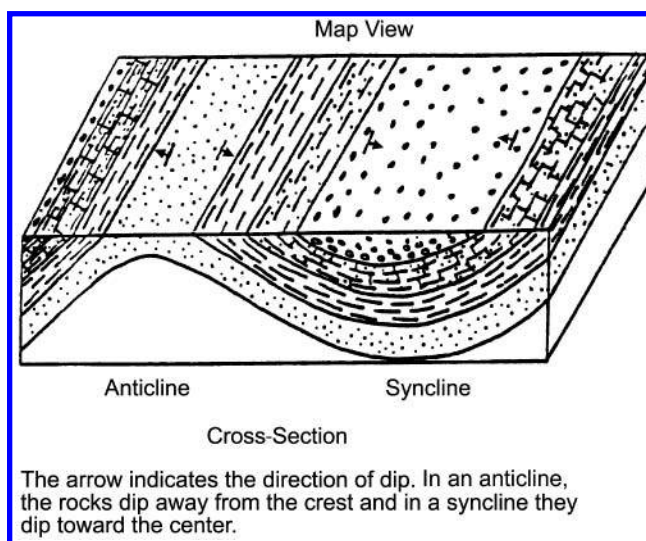


Figure 1.4 Block diagram of an anticline and syncline (U.S. EPA, 1987a).

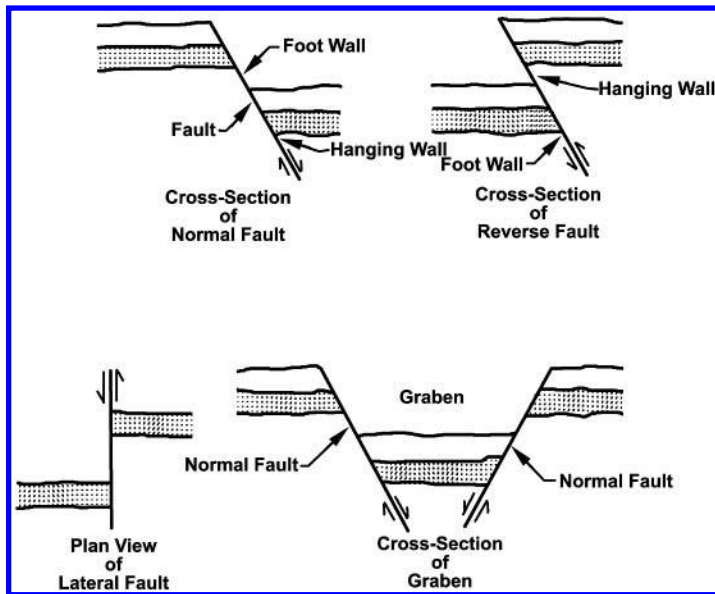


Figure 1.5 Cross sections of normal and reverse faults and a graben; plan view of a lateral fault (U.S. EPA, 1987a).

dip and strike symbols. The strike is perpendicular to the dip, and dip is commonly recorded as the number of degrees with respect to the horizontal plane. The dip may range from less than a degree to vertical.

Fractures. Fractures in rocks are either joints or faults. A *joint* is a fracture along which no movement has taken place; a *fault* implies movement. Movement along faults is as little as a few inches to tens of miles. Probably all consolidated rocks and a good share of the unconsolidated deposits contain joints. Joints exert a major control on ground-water movement and chemical quantity. Characteristically, joints are open and serve as major conduits or pipes. Water can move through them quickly, perhaps carrying contaminants, and being open, the filtration effect is lost. The outbreak of many waterborne diseases can be traced to ground-water supplies containing infectious agents that have been transmitted through fractures to wells and springs.

Faults are most common in the deformed rocks of mountain ranges, suggesting either lengthening or shortening of the crust. Movement along a fault may be horizontal, vertical, or a combination of both. The most common types of faults are called normal, reverse, and lateral (Figure 1.5). A *normal* fault, which indicates stretching of the crust, is one in which the upper or hanging wall has moved down relative to the lower or footwall.

Death Valley in California, the Red Sea, and the large lake basins in the east African highlands, among many others, lie in a *graben*, which is a block bounded by normal faults (Figure 1.5). A *reverse* or *thrust* fault implies compression and shortening of the crust. It is distinguished by the fact that the hanging wall has moved up relative to the footwall. A *lateral* fault is one in which the movement has been largely horizontal. The San Andreas Fault, extending some 600 mi from San Francisco Bay to the Gulf of California, is the most notable lateral fault in the U.S.

1.3.4 Geologic Maps and Cross Sections

Geologists use a number of techniques to graphically represent surface and subsurface conditions. Some of the more important methods that may have value in ground-water investigations are described here briefly:

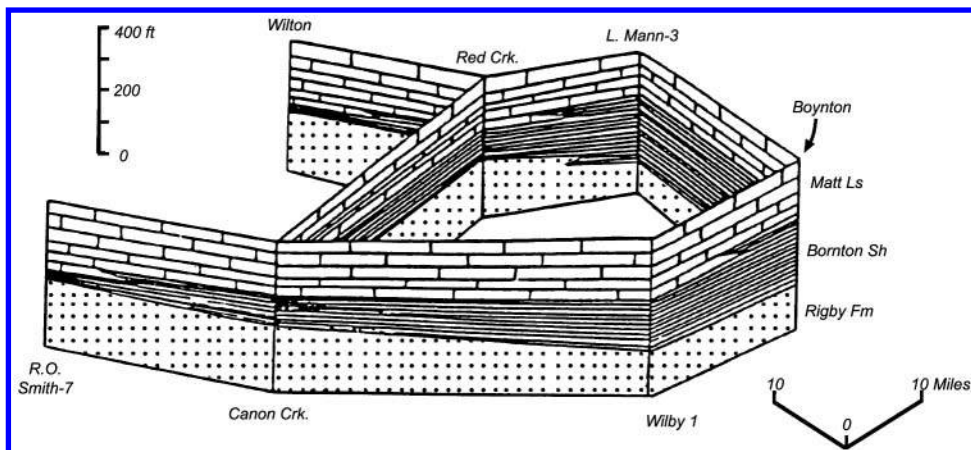


Figure 1.6 Sample fence diagram construction (Mercer and Spalding, 1991b, after Compton, 1962).

- *Surface geologic maps* depict the geographic extent of formations and their structure at the earth's surface. The map view portion of Figure 1.4 represents such a map.
- *Subsurface geologic maps* show the areal location of buried rock and other geologic units. These include (1) *structure contour* maps that show the elevation of a particular rock unit such as bedrock below glacial deposits or the top of a single rock formation; and (2) *isopach maps* that show variations in thickness of a unit and are based largely or entirely on well logs.
- *Cross sections* may take several forms: (1) *geologic cross sections*, which illustrate the subsurface distribution of rock units between points of control, such as outcrops or well bores; (2) *columnar sections*, which describe the vertical distribution of rock units, their lithology, and thickness; and (3) graphical representation of borehole logs without interpolation, as is required for geologic cross sections.
- *Three-dimensional* representations of geologic data can be accomplished by *block diagrams* (Figure 1.4) and *panel diagrams* (also called *fence diagrams*), in which cross sections are combined to create a three-dimensional image (Figure 1.6).

Whatever the graphic techniques, they are not exact because the features they attempt to show are complex, nearly always hidden from view, and difficult to sample. Nevertheless, graphic representations are valuable, if not essential, to subsurface studies.

1.4 BASIC SOIL CONCEPTS

Although the term *soil* is often loosely used to refer to any unconsolidated material, soil scientists distinguish it from other unconsolidated geologic materials by observable features that result from soil-forming processes, such as accumulation of organic matter, formation of soil structure, and leaching. Soil forms at the land surface in geologic materials, and consequently, the study of soil is at the interface between geology (particularly glacial and quaternary geology) and geomorphology.

1.4.1 Factors of Soil Formation

The soil at a particular location is the result of the interaction of five factors: (1) parent material, (2) topography, (3) climate, (4) biota, and (5) time:

- *Parent material*, in the form of unweathered consolidated or unconsolidated geologic material, provides the initial physical and chemical framework for soil formation.
- *Topography* affects soil formation by its influence on erosion and wetness. For example, soils on steep slopes tend to be thin and poorly developed because the rate of erosion tends to counterbalance the effects of weathering by climate and biota.

- *Climate* influences soil formation primarily by the amount of precipitation. Soils can be broadly classified based on the relationship between precipitation and evapotranspiration. In humid climates, where precipitation exceeds evapotranspiration, soluble constituents leach from the soil. Where evapotranspiration exceeds precipitation, as in arid and semiarid climates, salts tend to accumulate in the soil profile.
- *Biota* affects soil formation primarily through the process of organic matter formation. Vegetation is the major biological factor. For example, in the same parent material, prairie grassland will form an entirely different type of soil than a forest.
- The length of *time* that parent material is subjected to the weathering processes of climate and biological activity strongly influences soil type. A young soil in fresh geologic materials will look very different from a soil in the same material where weathering processes have operated for tens or hundreds of thousands of years.

The interaction of the above factors of soil formation results in the formation of a soil *profile*, the description of which forms the basis for classifying a soil. Specific soil-forming processes that influence soil profile development include (1) organic matter accumulation; (2) weathering of minerals to clays; (3) the depletion of clay and other sesquioxide minerals from upper horizons, called *eluviation*, with subsequent enrichment in lower horizons, called *illuviation*; (4) leaching or accumulation of soluble salts; (5) the formation of *soil structure* by the aggregation of soil particles into larger units called *peds*; and (6) the formation of slowly permeable layers, such as *fragipans* in humid climates and *duripans* in arid climates.

Perhaps the most distinctive feature of a soil profile is its major horizons:

- The *O horizon*, if present, is a layer of partially decomposed organic material.
- The *A horizon* is a mineral horizon characterized by maximum accumulation of organic matter lying at or near the ground surface. It usually has a distinctly darker color than lower horizons.
- The *E horizon*, whose main feature is the loss of silicate clay, iron, or aluminum, is typically found between the A and B horizons. (Note: Soil textbooks published before 1981 call this the B1 horizon.) It may also occur within a B horizon above a fragipan.
- The *B horizon* is the zone of most active weathering, is often enriched in clays, and has a well-defined soil structure. In humid climate soluble cations, such as calcium, are often depleted, whereas in drier climates calcium carbonate and other soluble salts often accumulate in this horizon. Soil formed in recent geologic materials typically is missing a B horizon, or it is observable only by a slightly redder color compared to the C horizon.
- The *C horizon* is unconsolidated material that has experienced little or no weathering. In arid zones minerals may precipitate in the C horizon to form cemented petrocalcic layers (also called *caliche*) or duripans (cementation by silica).
- The *R horizon* is solid rock.

Depending on the interaction between the five factors of soil formation at a site, the transport of contaminants in the subsurface can be increased or decreased relative to unweathered materials with similar physical and chemical composition (Sections 1.4.3 and 1.4.4). Many soil properties that affect the potential for contaminant transport in the subsurface can be evaluated using soil profile descriptions, prepared using USDA soil description procedures. Section 1.7 identifies major references on these methods.

1.4.2 Soil Classification

The dominant system for classifying soils in the U.S. is the USDA soil taxonomy. This system went through seven “approximations” before being formalized in 1975 with the publication of *Soil Taxonomy* (Agricultural Handbook 436). The second edition was published in 1999 (Soil Survey Staff, 1999/T1.3). It is still an evolving system, which is updated biannually by the Soil Survey Staff of the Natural Resources Conservation Service (formerly called Soil Conservation Service (SCS)) in *Keys to Soil Taxonomy* (the ninth edition was published in 2002). Although the nomen-

clature may seem intimidating to the uninitiated, the USDA soil classification system is a very useful tool for assessing potential for transport of contaminants in the subsurface. The agricultural origins of the system resulted in a strong emphasis on features affecting soil water and nutrient status. These are the same soil properties that are most significant when evaluating soil and ground water contamination. The following is a brief overview of the system.

The USDA soil taxonomy is a hierarchical classification system with six levels:

- *Orders* and *suborders* form the highest level. The original system had 10 orders (see legend to [Figure 1.7](#)) and 47 suborders, which are differentiated by the presence or absence of diagnostic horizons and the kind and degree of dominant soil-forming processes. In 1990 an 11th order called *andosols* was added for soils formed in volcanic ashes.
- *Great groups* and *subgroups* are the next level. There are about 185 great groups and about 970 subgroups. Great groups are differentiated based on the whole assemblage of soils horizons and moisture and temperature regimes. Subgroups are defined based on significant subordinate soil processes that result in intergrades or transitional forms to other orders, suborders, or great groups.
- *Families* are a category within a subgroup that have similar physical and chemical properties, including (1) particle-size distribution, (2) mineralogy, (3) temperature regime, and (4) rooting depth. About 4500 families are currently recognized in the U.S.
- *Series* is the lowest category in the system and is defined by a more limited range of characteristics than the family grouping. Over 10,500 soil series have been recognized in the U.S. In soil mapping a soil series is further subdivided into *map units* reflecting occurrence on different slope classes and sometimes degrees of erosion. However, soil map units are not considered to be a level in the classification system.

Figure 1.7 shows the patterns of soil orders and suborders in the U.S. The legend describes their salient characteristics and the origin of major word roots. Familiarity with this system provides a powerful tool for interpreting soil conditions at any site where a soil survey conducted by the U.S. Soil Conservation Service (now Natural Resources Conservation Service) is available.

1.4.3 Soil Physical Properties

Soil physical properties such as texture (see [Section 1.1.2](#)), structure, and pore-size distribution are the major determinants in water movement in soil and, consequently, of major concern in ground-water contamination studies. Depending on the specific soil, water movement may be enhanced or retarded compared to unweathered geologic materials. Organic matter enhances water-holding capacity and infiltration. The formation of soil structure also enhances permeability, particularly in clayey soils. Buried soil horizons form zones of preferential lateral movement of contaminants in the subsurface, which may be overlooked by environmental professionals who are not trained to recognize such horizons. On the other hand, the formation of restrictive layers such as fragipans may substantially reduce infiltration compared to unweathered materials.

The study of soil water is primarily the domain of the soil physicist. Physical properties affecting movement of water in soil are discussed further in [Section 2.2.2](#) (Infiltration) and [Section 2.4](#) (Water in the Vadose Zone). Soil micromorphology and fabric analysis are methods for studying other soil physical properties. These methods typically involve the preparation of thin sections and examination of pores and other ordered features through a microscope.

Micromorphological and general fabric analysis of soil is used infrequently in the study of ground-water contamination, more because of unfamiliarity with the methods than their lack of value. For example, Collins and McGown (1981)² used micromorphologic and fabric analysis of layered alluvial soils and glacial soils to evaluate discontinuities for engineering purposes. Paglai

² Collins, K. and A. McGown. 1981. Micromorphological studies in soil engineering, in *Soil Micromorphology, Vol. 1. Techniques and Applications*, P. Bullock and C.P. Murphy, Eds., Academic Publishers, New York, pp. 195–217.

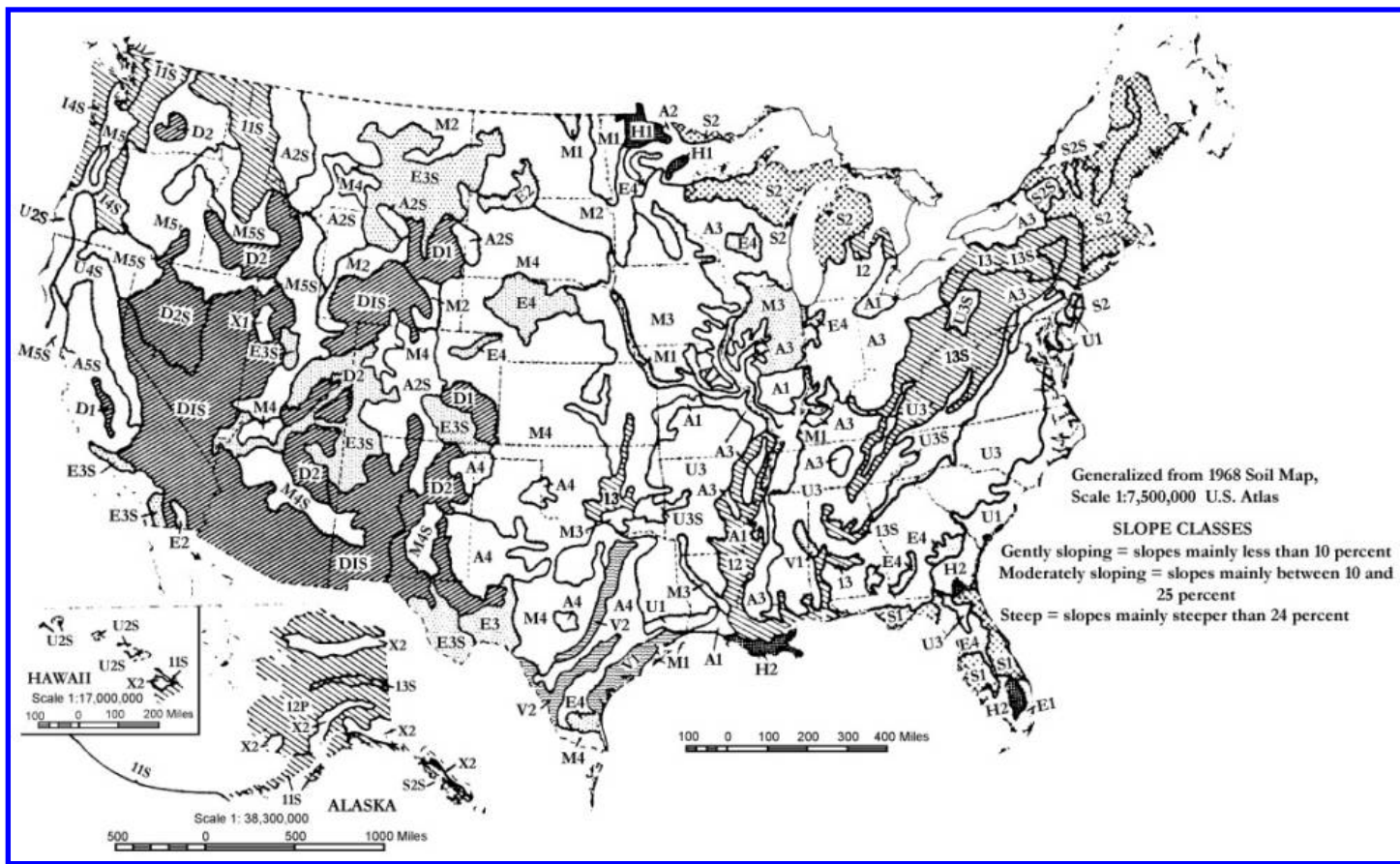







Figure 1.7 Patterns of soil orders and suborders of the U.S. (Birkeland, 1984).

Continued.

LEGEND	
<p>Only the dominant orders and suborders are shown. Each delineation has many inclusions of other kinds of soil. General definitions for the orders and suborders follow. For complete definitions, see Soil Survey Staff.¹² Approximate equivalents in the modified 1938 soil classification system are indicated for each suborder.</p>	
	ALFISOLS . . . Soils with gray to brown surface horizons, medium to high base supply, and subsurface horizons of clay accumulation; usually moist but may be dry during warm season
A1	AQUALFS (seasonally saturated with water) gently sloping; general crops if drained, pasture and woodland if undrained (Some Low-Humic Gley soils and Planosols)
A2	BORALFS (cool or cold) gently sloping; mostly woodland, pasture, and some small grain (Gray Wooded soils)
A2S	BORALFS steep; mostly woodland
A3	UDALFS (temperate, or warm, and moist) gently or moderately sloping; mostly farmed, corn, soybeans, small grain, and pasture (Gray-Brown Podzolic soils)
A4	USTALFS (warm and intermittently dry for long periods) gently or moderately sloping; range, small grain, and irrigated crops (Some Reddish Chestnut and Red-Yellow Podzolic soils)
A5S	XERALFS (warm and continuously dry in summer for long periods, moist in winter) gently sloping to steep; mostly range, small grain, and irrigated crops (Noncalcic Brown soils)
	ARIDISOLS . . . Soils with pedogenic horizons, low in organic matter, and dry more than 6 months of the year in all horizons
D1	ARGIDS (with horizon of clay accumulation) gently or moderately sloping; mostly range, some irrigated crops (Some Desert, Reddish Desert, Reddish Brown, and Brown soils and associated Solonetz soils)
D1S	ARGIDS gently sloping to steep
D2	ORTHIDS (without horizon of clay accumulation) gently or moderately sloping; mostly range and some irrigated crops (Some Desert, Reddish Desert, Sierozem, and Brown soils, and some Calcisols and Solonchak soils)
D2S	ORTHIDS gently sloping to steep
	ENTISOLS . . . Soils without pedogenic horizons
E1	AQUENTS (seasonally saturated with water) gently sloping; some grazing
E2	ORTHENTS (loamy or clayey textures) deep to hard rock; gently to moderately sloping; range or irrigated farming (Regosols)
E3	ORTHENTS shallow to hard rock; gently to moderately sloping; mostly range (Lithosols)
E3S	ORTHENTS shallow to rock; steep; mostly range
E4	PSAMMENTS (sand or loamy sand textures) gently to moderately sloping; mostly range in dry climates, woodland or cropland in humid climates (Regosols)
	HISTOSOLS . . . Organic soils
H1	FIBRISTS (fibrous or woody peats, largely undecomposed) mostly wooded or idle (Peats)
H2	SAPRISTS (decomposed mucks) truck crops if drained, idle if undrained (Mucks)
	INCEPTISOLS . . . Soils that are usually moist, with pedogenic horizons of alteration of parent materials but not of accumulation
I1S	ANDEPTS (with amorphous clay or vitric volcanic ash and pumice) gently sloping to steep; mostly woodland; in Hawaii mostly sugar cane, pineapple, and range (Ando soils, some Tundra soils)
I2	AQUEPTS (seasonally saturated with water) gently sloping; if drained, mostly row crops, corn, soybeans, and cotton; if undrained, mostly woodland or pasture (Some Low-Humic Gley soils and Alluvial soils)

(continued)

Figure 1.7 Legend.





12P AQUEPTS (with continuous or sporadic permafrost) gently sloping to steep; woodland or idle (Tundra soils)	S1 AQUODS (seasonally saturated with water) gently sloping; mostly range or woodland; where drained in Florida, citrus and special crops (Ground - Water Podzols)
13 OCHREPTS (with thin or light-colored surface horizons and little organic matter) gently to moderately sloping; mostly pasture, small grain, and hay (Sols Bruns Acides and some Alluvial soils)	S2 ORTHODS (with subsurface accumulations of iron, aluminum, and organic matter) gently to moderately sloping; woodland, pasture, small grains, special crops (Podzols, Brown Podzolic soils)
13S OCHREPTS gently sloping to steep; woodland, pasture, small grains	S2S ORTHODS steep; mostly woodland
14S UMBREPTS (with thick dark-colored surface horizons rich in organic matter) moderately sloping to steep; mostly woodland (Some Regosols)	 ULTISOLS . . . Soils that are usually moist, with horizon of clay accumulation and a low base supply
 MOLLISOLS . . . Soils with nearly black, organic-rich surface horizons and high base supply	U1 AQUULTS (seasonally saturated with water) gently sloping; woodland and pasture if undrained, feed and truck crops if drained (Some Low - Humic Gley soils)
M1 AQUOLLS (seasonally saturated with water) gently sloping; mostly drained and farmed (Humic Gley soils)	U2S HUMULTS (with high or very high organic matter content) moderately sloping to steep; woodland and pasture if steep, sugar cane and pineapple in Hawaii, truck and seed crops in Western States (Some Reddish-Brown Lateritic soils)
M2 BOROLLS (cool or cold) gently or moderately sloping, some steep slopes in Utah; mostly small grain in North Central States, range and woodland in Western States (Some Chernozems)	U3 UDULTS (with low organic-matter content; temperate or warm, and moist) gently to moderately sloping; woodland, pasture, feed crops, tobacco, and cotton (Red-Yellow Podzolic soils, some Reddish-Brown Lateritic soils)
M3 UDOLLS (temperate or warm, and moist) gently or moderately sloping; mostly corn, soybeans, and small grains (Some Brunizems)	U3S UDULTS moderately sloping to steep, woodland, pasture
M4 USTOLLS (intermittently dry for long periods during summer) gently to moderately sloping; mostly wheat and range in western part, wheat and corn or sorghum in eastern part, some irrigated crops (Chestnut soils and some Chernozems and Brown soils)	U4S XERULTS (with low to moderate organic-matter content, continuously dry for long periods in summer) range and woodland (Some Reddish-Brown Lateritic soils)
M4S USTOLLS moderately sloping to steep; mostly range or woodland	 VERTISOLS . . . Soils with high content of swelling clays and wide deep cracks at some season
M5 XEROLLS (continuously dry in summer for long periods, moist in winter) gently to moderately sloping; mostly wheat, range, and irrigated crops (Some Brunizems, Chestnut, and Brown soils)	V1 UDERTS (cracks open for only short periods, less than 3 months in a year) gently sloping; cotton, corn, pasture, and some rice (Some Grumusols)
M5S XEROLLS moderately sloping to steep; mostly range	V2 USTERTS (cracks open and close twice a year and remain open more than 3 months); general crops, range, and some irrigated crops (Some Grumusols)
 SPodosOLS . . . Soils with accumulations of amorphous materials in sub-surface horizons	

Figure 1.7 Legend.


	AREAS with little soil . . .	bor	— Gr. <i>boreas</i> , northern; cool
X1	Salt flats X2	fibr	— L. <i>fibra</i> , fiber; least decomposed
X2	Rock land (plus ice fields in Alaska)	hum	— L. <i>humus</i> , earth; presence of organic matter
NOMENCLATURE			
The nomenclature is systematic. Names of soil orders end in <i>sol</i> (L. <i>solum</i> , soil), e.g., ALFISOL, and contain a formative element used as the final syllable in names of taxa in suborders, great groups, and subgroups.			
Names of suborders consist of two syllables, e.g., AQUALF. Formative elements in the legend for this map and their connotations are as follows:			
and	— Modified from Ando soils; soils from vitreous parent materials	ochr	— Gr. base of ochros, pale; soils with little organic matter
aqu	— L. <i>aqua</i> , water; soils that are wet for long periods	orth	— Gr. <i>orthos</i> , true; the common or typical
arg	— Modified from L. <i>argilla</i> , clay; soils with a horizon of clay accumulation	psamm	— Gr. <i>psammos</i> , sand; sandy soils
		sapr	— Gr. <i>sapros</i> , rotten; most decomposed
		ud	— L. <i>udus</i> , humid; of humid climates
		umbr	— L. <i>umbra</i> , shade; dark colors reflecting much organic matter
		ust	— L. <i>ustus</i> , burnt; of dry climates with summer rains
		xer	— Gr. <i>xeros</i> , dry; of dry climates with winter rains

Figure 1.7 Legend.

et al. (1981)³ used micromorphological methods to evaluate the effect of sewage sludges applied to soil on pore size and density.

1.4.4 Soil Chemical Properties

Minerals in the soil are the chemical signature of the bedrock from which they originated. Rainfall and temperature are two significant factors that dictate the rate and extent to which mineral solids in the soil react with water. As water passes through soil horizons, it dissolves the chemical remnants of the parent material. In arid and semiarid climates dissolved constituents often precipitate in a lower horizon when plants transpire soil water to the atmosphere. In humid climates, soil water that is not taken up by plant roots carries the dissolved minerals to the ground water. The more water that flows through the soil, the more solids react with the undersaturated solvent.

Organic matter and clay content are major parameters of importance in studying the transport and fate of contaminants in soil. The geochemical properties of clay have been described in [Section 1.1.1](#), and the importance of organic matter in adsorption of organic chemicals covered in [Section 3.4.4](#). Chapter 3 covers basic concepts related to soil chemistry.

1.5 GEOMORPHOLOGY AND GROUND WATER

Geomorphology is the study of the evolution of surface landforms. Careful observation of surface features at a site (landforms, streams and stream patterns, locations of springs, seeps, and lakes, as well as vegetation) may reveal considerable information about both geology and ground water. Landforms are controlled by the geology, and many hills are capped by resistant strata, such as sandstone, while valleys are usually carved into soft, less resistant material, such as shale.

³ Paglai, M., M. LaMarca, and G. Lucamante. 1981. Micromorphological investigation of the effect of sewage sludges applied to soil in *Soil Micromorphology, Vol. 1. Techniques and Applications*, P. Bullock and C.P. Murphy, Eds., Academic Publishers, New York, pp. 219–225.

Likewise, many changes in topographic slope are related to differences in rock type. These, in turn, provide a general impression of the types of rocks present, their areal extent, and composition. Rock exposures in stream channels and road cuts are very useful also when attempting to understand the local geology. Large-scale fracture systems can be mapped as linear features on aerial photographs. Lineations on aerial photographs may also serve as indicators of changes in lithology and geologic structure. At a smaller scale, joint and fracture systems, their directional trends, density, and size can all be measured on rock outcrops. Fluid movement through joints and other fractures may be the controlling factor for migration of contaminants.

Geomorphology is a logical starting point for site investigations, because it allows preliminary interpretations of subsurface conditions without the cost of drilling or other subsurface investigation methods. For example, Hatheway and Bliss (1980)⁴ used surficial geologic maps to develop geomorphic units of similar engineering and hydrogeologic properties as a starting point for evaluating siting options for hazardous waste facilities.

1.5.1 Hydrogeomorphology

A lot can be inferred about subsurface flow of water from examination of a topographic map, because slope steepness and shape strongly influence how much precipitation enters the ground. [Figure 1.8](#) illustrates a number of geomorphic and hillslope components. Refer to this figure for help in visualizing the following common relationships between surface runoff or infiltration (the entry of water into the soil) and geomorphic and hillslope features:

- *Headslopes* concentrate surface runoff; *noseslopes* disperse surface runoff.
- Infiltration is usually highest on *footslopes* and *toeslopes*, followed by interfluvies/hill summits, and lowest on shoulders and backslopes. At all topographic situations, infiltration is highest in dry soils and slows as the soil gets wetter.
- Surface runoff is usually greatest on steep surfaces such as *headslopes/sideslopes* and *shoulders/backslopes*, and lowest on flat surfaces (broad interfluvies and alluvial fill). At all topographic positions surface runoff is at a maximum when the soil is saturated.
- A *concave* sideslope will concentrate water in the soil more than a *convex* sideslope (this is not explicitly illustrated in Figure 1.8, but the principle is the same as the headslope/hillslope relationship).
- Alluvial fill will usually have more ground water than interfluvies.

The above relationships can be useful in developing a preliminary conceptual model of how water is flowing in the subsurface. Very subtle changes in surface topography may affect the distribution of water between the surface and ground. These are often evident in vegetation, with relative greenness marking differences in the availability of ground water. Vegetation can sometimes also be used to map certain rock types. For example, cedar trees can be an indicator of limestone bedrock. Springs and seeps are zones of ground-water discharge. They develop in the vicinity of strata of low permeability that are overlain by a unit of greater permeability.

Stream patterns also are related to the geology, especially geologic structure and fracture or joint systems. Regional stream patterns provide an idea of the relative difference in discharge from one stream to another. Surface streams can also provide useful information on basin permeability, shallow ground-water quality, and local sites where the ground water is contaminated (Section 2.3).

1.5.2 Karst Geomorphology and Hydrology

The term *karst*, named after the Dinaric karst limestone region of the former Yugoslavia, refers to a distinctive set of geomorphic landforms resulting from the development of extensive subsurface

⁴Hatheway, A.W. and Z.F. Bliss. 1980. Geomorphology as an aid to hazardous waste facility siting, Northeast United States, in *Applied Geomorphology*, R.G. Craig and J.L. Craft, Eds., George Allen & Unwin, Boston, MA, pp. 55–71.

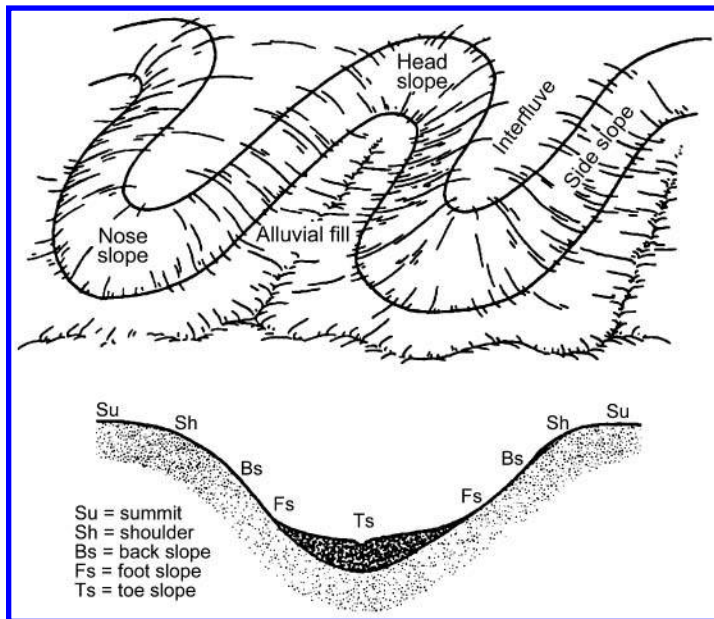


Figure 1.8 Geomorphic and hill slope components (Mausbach and Nielsen, 1991, after Ruhe and Walker, 1968).

solution channels and caves in carbonate rocks. These channels form where circulating ground water has dissolved carbonates along fractures and bedding planes (see [Figure 1.9](#)). Karst terrane (also spelled terrain in the karst literature) is usually characterized by sinkholes and general absence of perennial surface streams. Springs are abundant where impermeable rock below the cavernous limestone crops out at the surface.

Conduit flow, which does not obey Darcy's law (Section 2.6.3), is a salient characteristic of karst aquifers. As the term implies, flow in solution channels is rapid, more like flow in a pipe or open channel. This feature of karst aquifers makes them characteristically idiosyncratic in behavior, and surface water entering such a system may reappear at unexpected locations and at different locations depending on whether low- or high-flow conditions exist. As shown in [Figure 1.9](#), large fluctuations can result in seasonal artesian conditions. Ground-water tracing experiments are the only way that karst ground-water flow patterns can be accurately characterized (Section 8.4).

Karst areas are troublesome water sources even though they can provide large quantities of water to wells and springs. Rapid infiltration rates limit filtering action to retard contaminants; pollutants move rapidly once they reach a karst conduit and are less attenuated by adsorption compared to porous aquifers (Field, 1989).⁵ Consequently, karst terrane is generally unsuitable for the disposal of polluting wastes.

[Figure 1.10](#) shows the distribution of karst areas in the U.S. Near-surface karst areas are shaded, and other areas with carbonate or sulfate rocks near the surface are stippled. Karst areas in this figure are divided into four major regions: A = Atlantic and Gulf Coastal Plain; B = east-central region of Paleozoic and other old rock; C = Great Plains; and D = western mountain region. The distinctive geomorphic and hydrogeologic features of karst terrane have resulted in a scientific literature that is probably out of proportion to its actual distribution on the face of the earth (see next section).

⁵ Field, M.S. 1989. The Vulnerability of Karst Aquifers to Chemical Contamination. In: Recent Advances in Ground-Water Hydrology, J.E. Moore et al. (eds.), American Institute of Hydrology, Minneapolis, pp. 130–142.

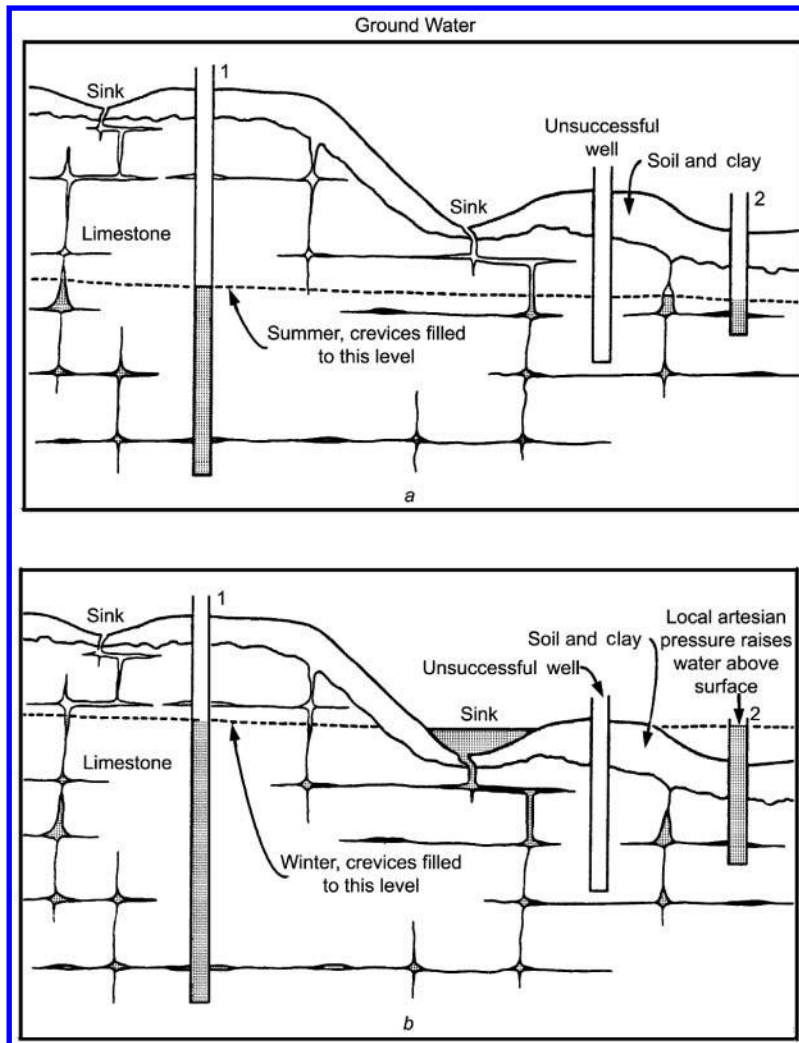


Figure 1.9 Diagram of a karst aquifer showing seasonal artesian conditions (Walker, 1956).

1.6 GEOLOGIC SETTINGS OF GROUND WATER OCCURRENCE AND QUALITY

The occurrence of ground water is intimately related to its geologic setting. Heath (1982)⁶ describes 12 major ground-water regions in the continental U.S. based on geologic setting: (1) Western mountain ranges, (2) alluvial basins, (3) Columbia lava plateau, (4) Colorado Plateau and Wyoming, (5) high plains, (6) nonglaciaded central region, (7) glaciaded central region (Figure 1.3), (8) Piedmont Blue Ridge region, (9) northeast and superior uplands, (10) Atlantic and Gulf Coastal Plain, (11) southeast coastal plain, and (12) alluvial valleys. Figure 1.11 shows the boundaries of the first 11 regions. The alluvial valleys region consists mainly of the floodplains of the Mississippi, Missouri, and Ohio Rivers. Aller et al. (1987/T11.10) have further subdivided Heath's major regions into 85 subregions for purposes of evaluating ground-water pollution potential. Section 11.2.3 discusses ground-water vulnerability mapping further.

⁶ Heath, R.C. 1982. Classification of Ground-Water Systems of the United States. *Ground Water* 20(4):393–401. Additional information on Heath's ground water regions can be found in U.S. Geological Professional Paper 2242, published in 1984.

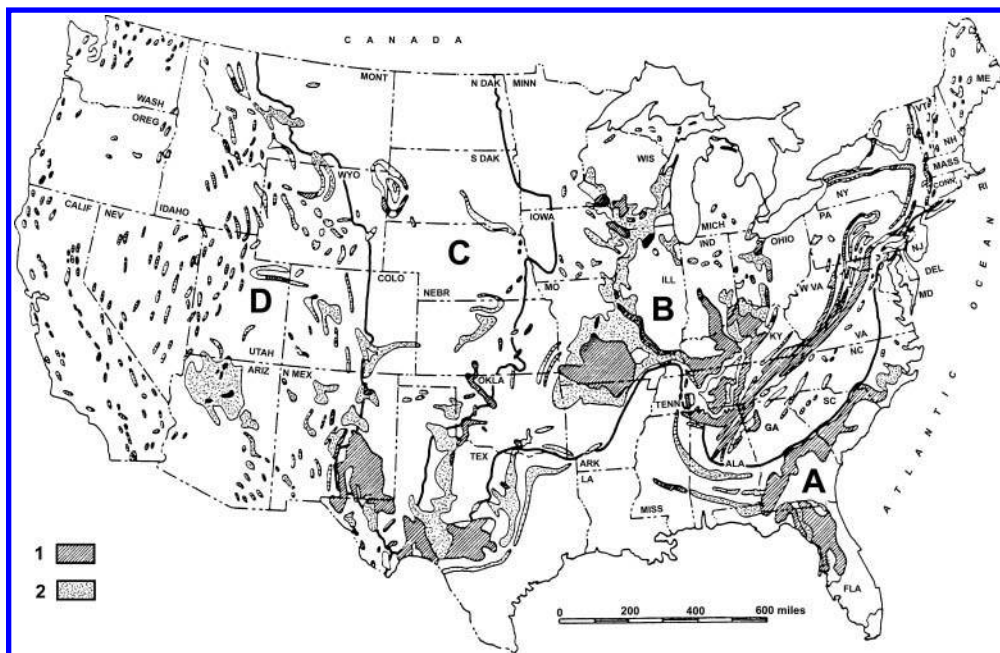


Figure 1.10 Distribution of karst areas in relation to carbonate and sulfate rocks in the U.S. (Davies and LeGrand, 1972). 1 = Karst areas; 2 = carbonate and sulfate rocks at or near the surface.

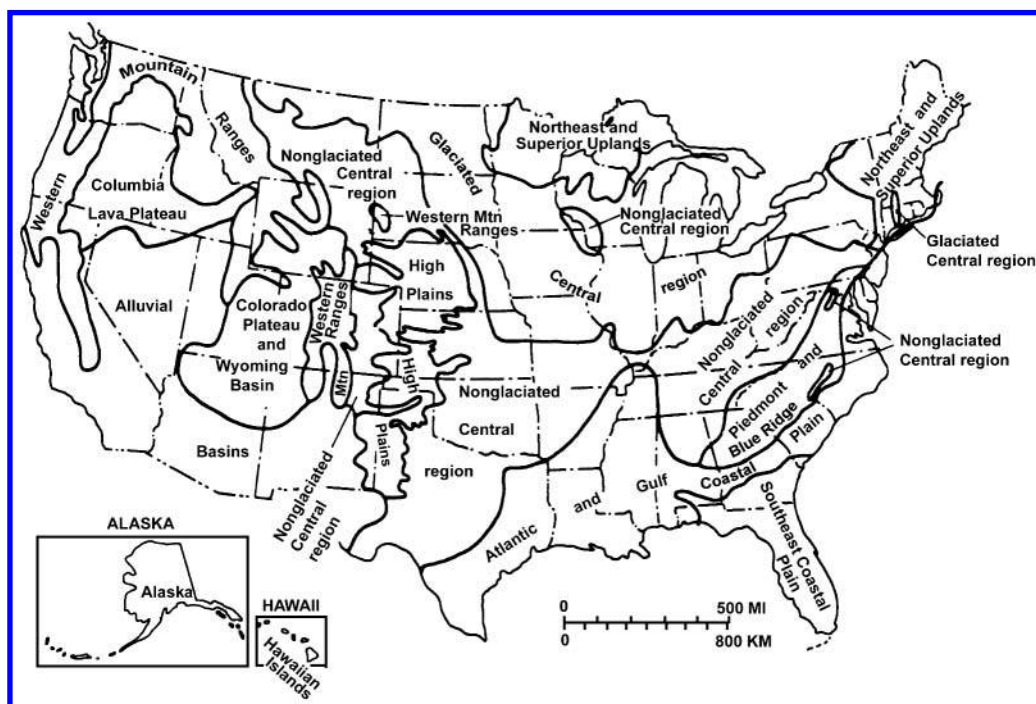


Figure 1.11 Major ground-water regions of the U.S. (Heath, 1984).

1.6.1 Ground Water in Igneous and Metamorphic Rocks

Nearly all of the porosity and permeability of igneous and metamorphic rocks are the result of secondary openings such as fractures and faults and the dissolution of certain minerals. A few notable exceptions include large lava tunnels present in some flows, interflow or coarse sedimentary layers between individual lava flows, and deposits of selected pyroclastic materials.

Because the openings in igneous and metamorphic rocks are quite small volumetrically, rocks of this type are poor suppliers of ground water. The supplies that are available commonly drain rapidly after a period of recharge by infiltration of precipitation. In addition, they are subject to contamination from the surface where these rocks outcrop.

Evaluating water and contaminant movement in fractured rocks is difficult, because the actual direction of movement may not be in the direction of decreasing head, but rather in some different though related direction. The problem is further compounded by the difficulty in locating the fractures. Because of these characteristics, evaluating water availability, direction of movement, and velocity is exceedingly difficult.

Unless some special circumstance exists, such as where rocks crop out at the surface, water obtained from igneous and metamorphic rocks is nearly always of excellent chemical quality. Dissolved solids are present in crystalline rocks; however, they are commonly in concentrations of less than 100 mg/l. In the case of water from metamorphosed carbonate rocks, moderate to high concentrations of hardness may be found.

1.6.2 Ground Water in Sedimentary Rocks

Usable supplies of ground water can be obtained from all types of sedimentary rocks, but the fine-grained strata such as shale and siltstone may only provide a few gallons per day, and even this can be highly mineralized. Even though fine-grained rocks may have relatively high porosities, their primary permeabilities are usually low. On the other hand, shale is likely to contain a great number of joints that are closely spaced and extend to considerable depths. Therefore, in this case, rather than being impermeable, they can be quite transmissive. This is of considerable importance in waste disposal schemes because of the potential for flow through fractures. In addition, leachate formed as water infiltrates through waste might be small in quantity but highly mineralized. Because of the low bulk permeability, it would be difficult to pump out the contaminated water or even to properly locate monitoring wells.

From another perspective, fine-grained sedimentary rocks, owing to their high porosity, can store huge quantities of water. Some of this water can be released to adjacent aquifers when a head difference is developed due to pumping. On a regional scale, fine-grained confining units provide a great deal of water to aquifer systems. The porosity, however, decreases with depth because of compaction brought about by the weight of overlying sediments.

The porosity of sandstones ranges from less than 1% to a maximum of about 30%. This is a function of sorting, grain shape, and cementation. Cementation can vary both in space and time, and on outcrops, cementation can differ greatly from that in the subsurface.

As is the case in igneous and metamorphic rocks, fractures also play an important role in the movement of fluids through sandstones. Transmissivities may be as much as two orders of magnitude greater in a fractured rock than in an unfractured part of the same geologic formation.

Sandstone units that were deposited in a marine or near-marine environment can be very widespread, covering tens of thousands of square miles, such as the St. Peter Sandstone of the Cambrian age. Those representing ancient alluvial channel fills, deltas, and related environments of deposition are more likely to be discontinuous and erratic in thickness. Individual units are exceedingly difficult to trace in the subsurface. Regional ground-water flow and storage may be strongly influenced by the geologic structure.

Carbonate rocks are formed in many different environments, and the original porosity and permeability are modified rapidly after burial. Some special carbonate rocks, such as coquina and some breccias, which tend to have a coarse texture, may remain very porous and permeable, but these are exceptions. When calcite changes to dolomite ($\text{CaMg}(\text{CO}_3)_2$), the resulting 13% reduction in volume creates considerable pore space. High-yielding aquifers develop from fractures and other secondary openings in carbonate formations (see discussion of karst in [Section 1.5.2](#)).

1.6.3 Ground Water in Unconsolidated Sediments

Unconsolidated sediments accumulate in many different environments, all of which leave their mark on the characteristics of the deposit. Some are thick and areally extensive, as the alluvial fill in the Basin and Range Province; others are exceedingly long and narrow, such as the alluvial deposits along streams and rivers; and others may cover only a few hundred square feet, for example, some glacial forms. In addition to serving as major aquifers, unconsolidated sediments are also important as sources of raw materials for construction.

Closely related to sorting, the porosities of unconsolidated materials range from less than 1% to more than 90%, the latter representing the porosity of uncompacted mud. Permeabilities also range widely. Cementing of some type and degree is probably universal, but not obvious, with silt and clay being the predominant form.

Most unconsolidated sediments owe their emplacement and texture (sorting, grain size, etc.) to running water. Water as an agent of transport varies in both volume and velocity, which are climate dependent, and this variation leaves an imprint on the sediments. Stream-related, unconsolidated material varies in extent, thickness, and grain size. The water-bearing properties of glacial drift are highly variable, but stratified drift is more uniform and better sorted than glacial till. Some knowledge of the stratigraphy of the most common depositional environments is essential for adequate characterization.

1.6.4 Regional Relationships in Ground-Water Quality

As water infiltrates in a recharge area, the mineral content is relatively low. The quality changes, however, along the flow path and dissolved solids as well as other constituents increase with increasing distances traveled in the ground. The water eventually flows into a stream or body of surface water, and due to the different lengths of flow paths and rock solubility, even streams and small lakes in close proximity may differ greatly in both flow and quality.

The availability of ground-water supplies and their chemical quality are closely related to precipitation. As a general rule, the least mineralized water, both in streams and underground, occurs in areas of the greatest amount of rainfall. Inland, precipitation decreases, water supplies diminish, and quality deteriorates. Because water-bearing rocks exert a strong influence on ground-water quality, however, the solubility of the rocks may override the role of precipitation.

Where precipitation exceeds 40 in. per year, shallow ground water usually contains less than 500 mg/l and commonly less than 250 mg/l of dissolved solids. Where precipitation ranges between 20 and 40 in., dissolved solids may range between 400 and 1000 mg/l, and in drier regions, dissolved solids commonly exceed 1000 mg/l.

The dissolved solids concentration of ground water increases toward the interior of the continent. The increase is closely related to precipitation and the solubility of the aquifer framework. The least mineralized ground water is found in a broad belt that extends southward from the New England states along the Atlantic Coast to Florida, and then continues to parallel much of the Gulf Coast. Similarly, along the Pacific Coast from Washington to central California the mineral content is also very low. Throughout this belt, dissolved solids concentrations are generally less than 250 mg/l and commonly less than 100 mg/l ([Figure 1.12](#)).

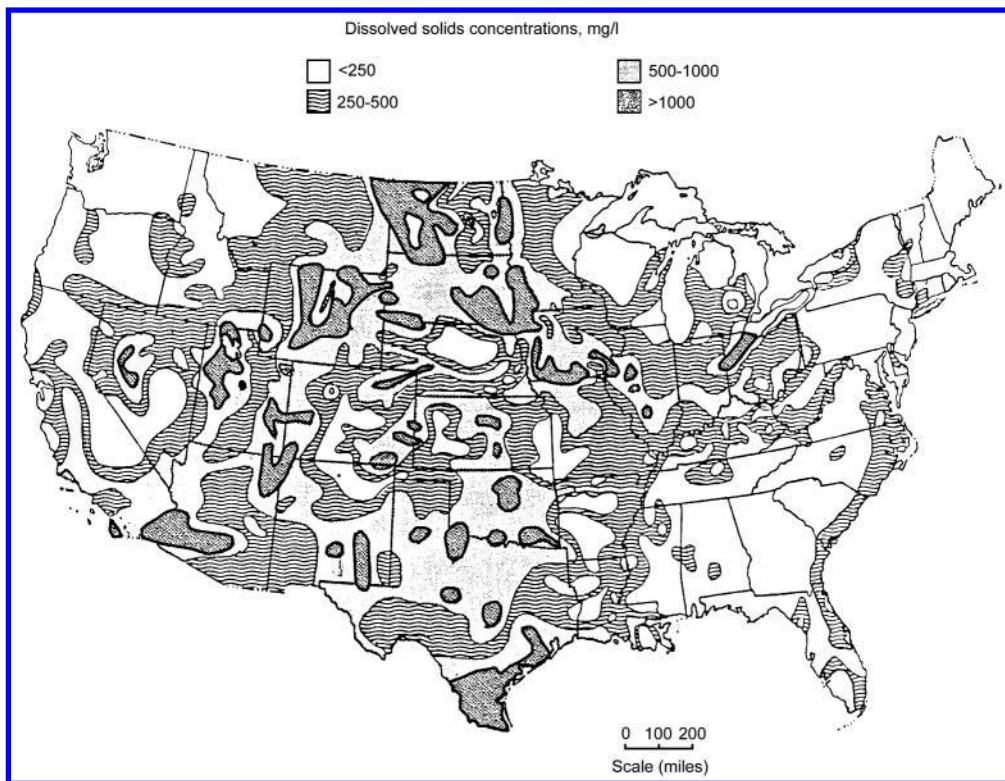


Figure 1.12 Dissolved solids concentrations in ground water used for drinking in the U.S. (U.S. EPA, 1987a, after Pettyjohn et al., 1979).

The Appalachian region consists of a sequence of strata that range from nearly horizontal to complexly folded and faulted. Likewise, ground-water quality in this region is also highly variable, being generally harder and containing more dissolved minerals than water along the coastal belt. Much of the difference in quality, however, is related to the abundance of carbonate aquifers, which provide waters rich in calcium and magnesium.

Westward from the Appalachian Mountains to about the position of the 20-in. precipitation line (eastern North Dakota to Texas), dissolved solids in ground water progressively increase. They are generally less than 1000 mg/l and are most commonly in the 250 to 750 mg/l range. The water is moderately to very hard, and in some areas concentrations of sulfate and chloride are excessive.

From the 20-in. precipitation line westward to the northern Rocky Mountains, dissolved solids are in the 500 to 1500 mg/l range. Much of the water from glacial drift and bedrock formations is very hard and contains significant concentrations of calcium sulfate. Other bedrock formations may contain soft sodium bicarbonate, sodium sulfate, or sodium chloride water.

Throughout much of the Rocky Mountains, ground-water quality is variable, although the dissolved solids concentrations commonly range between 250 and 750 mg/l. Stretching southward from Washington to southern California, Arizona, and New Mexico is a vast desert region. Here the difference in ground-water quality is wide and dissolved solids generally exceed 750 mg/l. In the central parts of some desert basins, the ground water is highly mineralized, but along the mountain flanks the mineral content may be quite low.

Extremely hard water is found over much of the interior lowlands, Great Plains, Colorado Plateau, and Great Basin. Isolated areas of high hardness are present in northwestern New York, eastern North Carolina, the southern tip of Florida, northern Ohio, and parts of southern California. In general, the hardness is of the carbonate type.

On a regional level, chloride does not appear to be a significant problem, although it is troublesome locally due largely to industrial activities, the intrusion of seawater caused by over-pumping coastal aquifers, or interaquifer leakage related to pressure declines brought about by withdrawals.

In many locations, sulfate levels exceed the federal recommended limit of 250 mg/l; regionally, sulfate may be a problem only in the Great Plains, eastern Colorado Plateau, Ohio, and Indiana. Iron problems are ubiquitous; concentrations exceeding only 0.3 mg/l will cause staining of clothing and fixtures. Fluoride is abnormally high in several areas, particularly parts of western Texas, Iowa, Illinois, Indiana, Ohio, New Mexico, Wyoming, Utah, Nevada, Kansas, New Hampshire, Arizona, Colorado, North and South Dakota, and Louisiana.

1.7 GUIDE TO MAJOR REFERENCES

[Table 1.3](#) identifies major text references in five major areas: (1) geology, (2) soils, (3) geomorphology, (4) interfaces between geology, soils, and geomorphology, and (5) engineering applications. The last category, soils and geologic engineering, has not been discussed in any detail in this chapter, but is an essential element in planning and design for remediation of contaminated soils and ground water.

Almost any text on physical geology, stratigraphy, and structural geology, general soils, and geomorphology will provide more in-depth coverage of topics covered in this chapter, but generally will not emphasize principles as they relate to soil and ground-water contamination. This chapter has emphasized the value of USDA Soil Conservation Service (now called the Natural Resources Conservation Service) soil description and survey methods for contaminant investigations, and more needs to be said about key reference sources in this area.

For years the standard reference for soil horizon nomenclature was the 1962 supplement to the *Soil Survey Manual* (Soil Survey Staff, 1951, 1962), and it was elaborated further in *Soil Taxonomy* (Soil Survey Staff, 1975, 1999).⁷ In 1981 conventions for describing soil horizons and subordinate distinctions within master horizons were significantly changed as part of a comprehensive revision of the 1951 *Soil Survey Manual*, which was published in 1994 (Soil Survey Staff, 1994). The best up-to-date source of official SCS horizon designations and naming conventions can be found in *Keys to Soil Taxonomy* (Soil Survey Staff, 2002), which is updated biannually.

None of the above documents are specifically oriented toward use of SCS soil description at contaminated sites. In 1991 U.S. EPA's Center for Environmental Research Information published *Description and Sampling of Contaminated Soils: A Field Pocket Guide* (Boulding, 1991), which presented a detailed, field-oriented adaptation of SCS soil description procedures for use with EPA's *Environmental Sampling Expert Systems* (Cameron, 1991). A second edition of the 1991 guide was published three years later (Boulding, 1994), which incorporated new SCS procedures for describing soil wetness conditions. These were adopted in 1992 and represent a significant improvement in the ability to characterize soil hydrology based on soil morphology. Burden and Sims (1999/T1.3) provide guidance on use of both the USDA and the more engineering-oriented ASTM Unified Soil Classification System at hazardous waste sites.

[Table 1.4](#) provides an index of major references on karst in the following categories: (1) hydrology and ground water, (2) karst tracing, (3) geomorphology and geology, (4) geochemistry, (5) engineering applications, (6) environmental applications, and (7) major symposia. Ford and Williams (1989) is probably the best single text that covers both karst geomorphology and hydrology with a strong U.S. focus. Balkema Publishers (Old Post Road, Brookfield, VT 05036) is the major publisher of conference proceedings related to karst hydrogeology.

⁷ Citations are to references included in Table 1.3.

Table 1.3 Index to Major References on Geology, Soils, and Geomorphology

Topic	References
Geology	
Terminology	Allaby and Allaby (1990), Bates and Jackson (1984), Michel and Fairbridge (1992), SCS (1977), Weller (1960a), Whitten and Brooks (1972)
Physical Geology	Birkeland and Larson (1989), Dercourt and Pacquet (1985), Flint and Skinner (1977), Foster (1983), Gilluly et al. (1975), Hamblin (1978), Mears (1977), Press and Siever (1986), Sawkins et al. (1978), Strahler (1976), Tarbuck and Lutgens (1984), Verhoogen et al. (1979)
Stratigraphy	Adams and Mackenzie (1999), Blatt et al. (1980), Bouma (1969), Chakraborty and Bhattacharyya (2000), Folk (1968), Garrels and Mackenzie (1971), Krumbein and Sloss (1963), Lucchi (1995), Matthews (1984), Pettijohn (1975), Pettijohn et al. (1987), Trask (1950), Weller (1960b)
Structural Geology	Billings (1972), Hills (1972), Ragan (1973), Ramsay and Huber (1983, 1987), Spencer (1977)
Field Geology	Bishop (1960), Compton (1962, 1985), Dietrich et al. (1990), Kempton (1981), Lahee (1961), LeRoy et al. (1987), Low (1957); <u>Field Rock Description</u> : Fry (1984), Thorpe and Brown (1985), Tucker (1982)
Soils	
General	Brady and Weil (1999), Charman and Murphy (2000), Courtney and Trudgill (1984), Fairbridge and Finkl (1979), Fitzpatrick (1980, 1986), Foth (1971), Harpstead and Hole (1980), Hausenbueller (1972), Jenny (1980), Singer and Munns (1999), Stefferud (1957), Sumner (2000), Van Breeman and Buurman (2001), Windegardner (1996); <u>Bedrock Soils</u> : Cremeens et al. (1994); <u>Forest Soils</u> : Armson (1979), Burns (1959), Lutz and Chandler (1947), Pritchett (1979), Valentine (1986), Wilde (1958); <u>Soil and Vegetation</u> : Trudgill (1988); <u>Wet Soils</u> : Rabenhorst et al. (1998), Richardson and Vepraskas (2000), Vepraskas and Sprecher (1997); <u>Terminology</u> : ASAE (1967), Gregorich et al. (2001), Soil Science Society of America (1996)
Classification and Mapping	Amundson et al. (1994), Bailey (1987 — bibliography), Buol et al. (1989), Butler (1980), Fanning and Fanning (1989), Finkl (1982), Forest Service (1961, 1963), McRae (1988), Milne et al. (1991), Olson (1981, 1984), Soil Survey Staff (1951, 1962, 1992, 1994, 1999, 2002), Webster (1977); <u>Contaminated Sites</u> : Boulding (1991, 1994), Burden and Sims (1999), Cameron (1991)
Micromorphology and Fabric Analysis	Brewer (1976), Brewer and Sleeman (1988), Bullock and Murphy (1983), Bullock et al. (1985), Douglas (1990), Douglas and Thompson (1985), Fitzpatrick (1984, 1993), Hartge and Stewart (1995-soil structure), Miedema and Mermut (1990), Stoops and Eswarin (1986), Thompson et al. (1993)
Geomorphology	
General	Chorley et al. (1984), Dury (1960), Lobeck (1939), Pitty (1971), Ritter (1986), Ruhe (1975), Selby (1985), Sparks (1986), Thornbury (1969); <u>Terminology</u> : SCS (1977)
Geomorphic Regions	Austin (1972), Fenneman (1931, 1938), Fenneman et al. (1946), Hunt (1967), Snead (1980), Thornbury (1965), USDA (1981)
Specific Topics	<u>Environmental</u> : Cook and Doornkamp (1990); <u>Coasts</u> : Trenhaile (1987); <u>Deserts</u> : Cook et al. (1993); <u>Fluvial</u> : Heede (1992), Leopold et al. (1964), Morisawa (1985), Richards (1982); <u>Ground Water</u> : Higgings and Coates (1990); <u>Hillslope</u> : Selby (1993); <u>Phytogeomorphology</u> : Howard and Mitchell (1985)
Interfaces between Geology, Soils, and Geomorphology	
Soils/Geomorphology	Birkeland (1999), Cruikshank (1972), Daniels and Hammer (1992), Foth and Shafer (1980), Gerrard (1981, 1992), Hole and Campbell (1981), Richards et al. (1985)
Glacial and Quaternary Soils/Geology/Geomorphology	Bell and Walker (1992), Catt (1986, 1988), Embleton and King (1968), Eyles (1983), Flint (1971), Ruhe (1965)

Table 1.3 Index to Major References on Geology, Soils, and Geomorphology (Continued)

Topic	References
Engineering Applications	
Soil	Asphalt Institute (1969), Bureau of Reclamation (1969, 1974, 1990), Chen (1999), Droshevskia (1962), Hough (1969), Kezdi (1980), Portland Cement Association (1992), SCS (1990), Sowers (1979), Terghazi and Peck (1967); <u>Unified Soil Classification System</u> : Howard (1986)
Soil Engineering Properties	Bell (1992), Bowles (1978, 1984), Lamb and Whitman (1969), Means and Parcher (1963), Mitchell (1976), Obert and Duvall (1967), Spengler and Handy (1982), Taylor (1948), U.S. Navy Facilities Command (1971), Yong and Wartentin (1975); <u>Foundation Engineering</u> : Bowles (1982), Leonards (1962), Peck et al. (1974)
Engineering Geology/Rock Mechanics	Attewell and Farmer (1976), Bell (1992), Bureau of Reclamation (1988, 1989), Dennen and Moore (1986), Heley and McIver (1971), Holtz and Kovacs (1981), Hunt (1972), Institution of Civil Engineers (1976), Legget and Hatheway (1988), Rahn (1986), Stagg and Zienkiewicz (1968); <u>Terminology</u> : International Society for Rock Mechanics (1972)

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* See Preface for information on how to obtain documents from CERI and NTIS.

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Topic	References
Glossary	Monroe (1970)
Hydrology/Ground Water	<u>Bibliographies</u> : LaMoreaux (1986), LaMoreaux et al. (1970, 1989, 1993), Warren and Moore (1975); <u>Texts</u> : Back et al. (1990), Bögli (1980), Bonacci (1987), Burger and Dubertret (1975), Ford and Williams (1989), LaMoreaux (1986), LaMoreaux et al. (1975, 1984), Milanović (1981), Stringfield et al. (1974), White (1988); <u>Review Papers</u> : Field (1989), Kresic (1993), LeGrand and Stringfield (1973); <u>Case Histories</u> : Burger and Dubertret (1984), White and White (1989); <u>Proceedings</u> : AGWSE (1991), Beck and Wilson (1987), Beck et al. (1999), Drew and Hötzl (1999), Doaxin (1988), Günay and Johnson (1986), IASH (1967), Rauch and Werner (1974), Saslowky and Wicks (2000), Tolson and Doyle (1977), Yevjevich (1976)
Karst Tracing	Aley and Fletcher (1976), Back and Zoetl (1975), Bögli (1980), Brown (1972), Ford and Williams (1989), Gospodaric and Habic (1976), Gunn (1982), Jones (1984), LaMoreaux (1984, 1989), Milanović (1981), Mull et al. (1988), Quinlan (1986, 1989), Sweeting (1973), SUWT (1966, 1970, 1976, 1981, 1986), Thraillkill et al. (1983)
Geomorphology/Geology	Dreybodt (1988), Ford and Williams (1989), Herak and Stringfield (1972), Jakucs (1977), Jennings (1985), Rauch and Werner (1974), Sweeting (1973), Trudgill (1985), White (1988)
Geochemistry	Dreybodt (1988)
Engineering Aspects	Davies et al. (1976), James (1992); <u>Proceedings</u> : Beck (1984, 1989), Beck and Wilson (1987), Beck et al. (1999)
Environmental Aspects	AGWSE (1991), Beck (1984, 1990), Beck and Wilson (1987), Doaxin (1988), NWWA (1986, 1988)
Conference Proceedings	AGWSE (1991), Beck (1984, 1990), Beck and Wilson (1987), Beck et al. (1999), Doaxin (1988), Drew and Hötzl (1999), Günay and Johnson (1986), IASH (1967), NWWA (1986, 1988), Rauch and Werner (1974), Saslowsky and Wicks (2000), Tolson and Doyle (1977), Yevjevich (1976)

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Ground Water and Vadose Zone Hydrology

Hydrogeology is the study of ground water — its origin, occurrence, movement, and quality. Modern hydrogeology in the past century has developed along three more or less separate lines:¹ (1) elaboration of the relation between geology and ground-water occurrences (Section 1.6), (2) development of mathematical equations to describe the movement of water through rocks and unconsolidated sediments (this chapter), and (3) the study of the chemistry of ground water (Chapter 3). Another line of study, movement of water in the *vadose*, or unsaturated zone, has been mainly studied by agronomists and soil physicists. Only in the last 10 years or so has the importance of the vadose zone in the study of the movement and fate of contaminants in the subsurface been recognized; this part of the ground-water system is still often overlooked.

2.1 GROUND WATER IN THE HYDROLOGIC CYCLE

The hydrologic cycle involves the continual movement of water between the atmosphere, surface water, and the ground ([Figure 2.1](#)). The ground-water system must be understood in relation to both surface water and moisture in the atmosphere. Most additions (recharge) to ground water come from the atmosphere in the form of precipitation, but surface water in streams, rivers, ponds, lakes, and artificial impoundments will move into the ground-water system wherever the hydraulic head of the water surface is higher than the water table ([Section 2.5.1](#)). Most water entering the ground as precipitation returns to the atmosphere by evapotranspiration before reaching the saturated zone. Most water that reaches the saturated zone eventually returns to the surface again by flowing to a point of discharge at the ground surface. Typically, these points of surface discharge are rivers, lakes, or the ocean; locally, they may also take the form of springs or soil seeps. Soil, geology, and climate will in large measure determine the amounts and rates of flow among the atmospheric, surface, and ground-water systems.

Ground water is the most difficult part of the hydrologic cycle to study because it is hidden from view and occurs in a complex environment of soil and geologic materials. The movement of water in the atmosphere and surface water can be directly observed, and boundary conditions (air–ground, air–surface water, and surface water–ground) are readily defined. Inferences concerning the movement of ground water rely largely on indirect observations supplemented by a limited number of direct observations (monitoring wells). Even data from direct observations may have large margins of error as a result of variability in the materials through which the ground water is flowing.

¹ Davis, S.N. and R.J.M. DeWiest. 1966. *Hydrogeology*. John Wiley & Sons, New York, 463 pp.

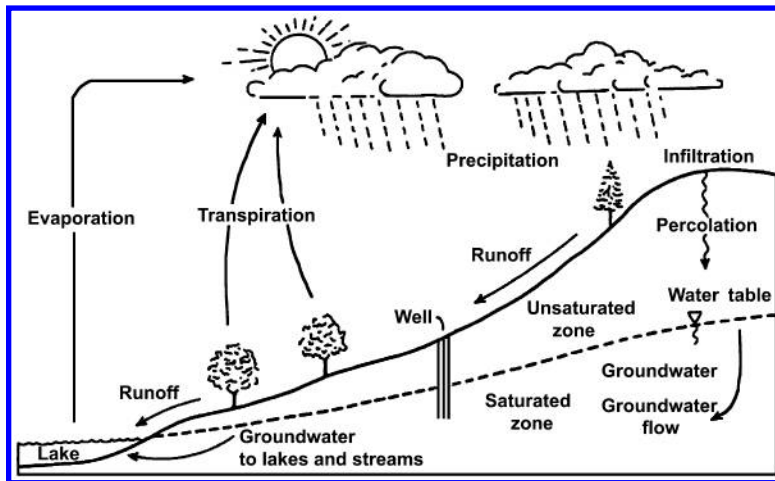


Figure 2.1 The hydrologic cycle (Muldoon and Payton, 1993).

Hydrogeology is not an exact science, but the fundamental principles of ground-water flow are well enough understood that a reasonably good characterization of a particular system is possible. In fact, at the site-specific level, the ground-water system is more predictable than either atmospheric or surface water systems that have large stochastic (random) elements. Provided that the subsurface system is adequately characterized, greater confidence can be placed in what direction and how far a contaminant will travel in a specified time period than in how much rain will fall or how much water will flow through a cross section of a stream during the same period of time.

2.2 GROUND WATER–ATMOSPHERIC RELATIONSHIPS

Precipitation, infiltration, and evapotranspiration are the key elements governing the flow of water between the atmosphere and the ground.

2.2.1 Precipitation

Precipitation (rain, snow, sleet, etc.) is usually the starting point of any mass balance analysis of the flow of water in the hydrologic cycle. Properties of precipitation that affect how much reaches the ground surface include:

- *Amount.* The total amount of precipitation falling on the surface is the first parameter required in any water budget calculation. There is likely to be more ground water, and it will tend to be nearer the surface, in an area of high precipitation rather than in one with low precipitation. [Figure 2.2](#) shows average annual precipitation in the continental U.S.
- *Form.* Whether precipitation reaches the ground as rain or snow will influence how much is likely to reach the ground-water system. In humid areas rain will more readily enter the soil than snow, although snow and ice may be significant sources of ground-water recharge in the spring once the ground has thawed. In arid, semiarid, and alpine areas snowmelt may be the dominant form of recharge to ground water.
- *Seasonal Distribution.* Equal amounts of precipitation during different seasons will result in different amounts of ground-water recharge. When the ground is frozen, ground-water recharge is low because snow returns to the atmosphere through evaporation or runs off the surface when it melts. In spring and early summer, when the ground is saturated or has a high moisture content, recharge will be the greatest. In late summer and fall, when soils tend to be drier, recharge will be less because precipitation goes to replenish soil moisture. Conversely, when plants are dormant

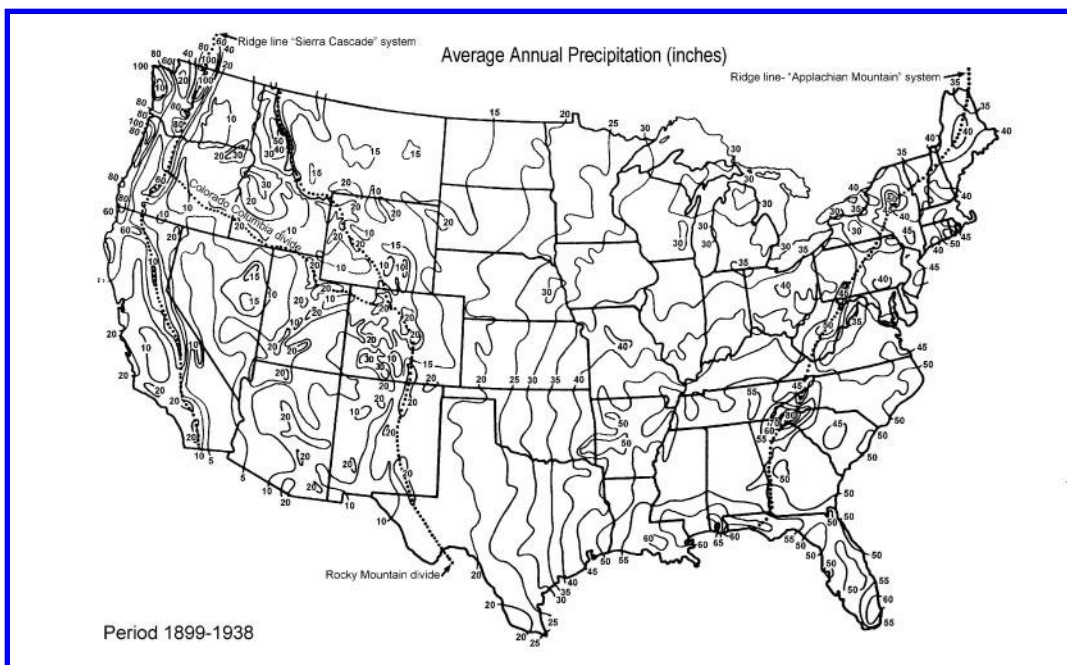


Figure 2.2 Mean annual precipitation (Viessman et al., 1972, after USDA Soil Conservation Service).

(i.e., after freeze in the fall, or in early spring before plants start their normal growth) recharge will be greater.

- **Intensity and Duration.** Precipitation events can be characterized by intensity (inches per hour) and duration (length of time over which the precipitation falls). *Convectonal* precipitation (thunderstorms with high intensity and short duration) is common during the summer and results in less ground-water recharge than *cyclonic* precipitation (low-intensity, long-duration events caused by large low-pressure systems that cross the U.S. from the northwest of the Gulf of Mexico). *Orographic* precipitation (caused by topographic barriers that force moisture-laden air to rise and cool) also tends to be of low intensity and long duration.

2.2.2 Infiltration

Not all precipitation reaches the ground; some is *intercepted* by buildings and trees and evaporates. The amount of water reaching the ground that then enters the soil is determined by the *infiltration capacity*. The infiltration capacity of a given soil is controlled by several factors:

- **Antecedent precipitation and soil moisture conditions.** Soil moisture fluctuates seasonally; it is usually high during winter and spring and low during the summer and fall. If the soil is dry, wetting the top of it will create a strong capillary potential just under the surface, supplementing gravity. When wetted, some clayey soils swell, closing pore spaces, thereby reducing the infiltration capacity shortly after a rain starts.
- **Compaction of the soil due to rain.** The impact of raindrops on the soil surface during an intense rainfall is more likely to reduce infiltration than a gentle rain.
- **Inwash of fine material** into soil openings reduces infiltration capacity. This is especially important if the soil is dry.
- **Compaction of the soil** due to animals, roads, trails, urban development, etc., reduces infiltration.
- Certain *microstructures* in the soil will promote infiltration, such as channels created by the interface between soil structural units; openings caused by burrowing animals, insects, decaying roots, and other vegetative matter; frost heaving; desiccation cracks; and other macropores.
- **Vegetative cover** tends to increase infiltration because it promotes populations of burrowing organisms and retards surface runoff, erosion, and compaction by raindrops.

- *Decreasing temperature*, which increases water viscosity, reduces infiltration.
- *Entrapped air* in the unsaturated zone tends to reduce infiltration.
- *Surface gradient*. Flat topography favors infiltration because any surface water will move more slowly than it will on sloping topography.

Infiltration capacity is usually greater at the start of a rain that follows a dry period, but it decreases rapidly. As the duration of rainfall increases, infiltration is determined by the saturated hydraulic conductivity of the soil and becomes nearly constant. In fine-grained soil, infiltration may be lower than the hydraulic conductivity immediately below the surface as a result of clogging by particles. If precipitation is greater than the infiltration capacity, surface runoff occurs. If it is less than the infiltration capacity, all the moisture enters the subsurface. The amount of infiltrating water that actually enters the ground-water system as recharge will depend on the amount of evapotranspiration.

2.2.3 Evapotranspiration

Water moves from the ground to the atmosphere by direct evaporation and by plant transpiration. During the growing season, water intercepted by vegetation before reaching the ground, which then evaporates, typically amounts to 10 to 20% of total precipitation in humid areas. Water removal from the soil by transpiration occurs to whatever depth plant roots are able to penetrate. Depending on the type of vegetation and soil conditions, this depth is typically 3 to 4 ft for grains and pasture grasses (although under favorable conditions, alfalfa roots will penetrate as deep as 10 ft). Deciduous trees have deeper roots and consequently remove soil moisture from greater depths (6 to 12 ft or more); desert plants may extend roots tens of feet below the surface to obtain moisture. Obviously, these rooting depths will be shallower where soil or geologic conditions limit rooting.

The relationship between evapotranspiration and precipitation determines whether soluble salts in soil will leach (precipitation > evapotranspiration) or accumulate (precipitation < evapotranspiration). This has important implications for contaminant transport, because a leaching environment will tend to move soluble contaminants into the saturated zone (generally in the humid East, Midwest, and coastal areas of the Pacific Northwest), whereas contaminants will tend to stay in the soil in a salt-accumulating environment (the semiarid plains and deserts of the West).

2.2.4 Distribution of Precipitation in the Hydrologic Cycle

Very little precipitation that reaches the ground surface actually reaches the saturated zone. The mass balance for precipitation at a site in southwestern Indiana might look something like this:

$$P = E + T + G + S \quad (2.1)$$

where:

P = precipitation = 41 in.

E = evaporation (interception) = 4 in.

T = transpiration = 24 in.

G = ground-water recharge = 1 in.

S = surface runoff = 12 in.

This example shows that about 10% of the precipitation is intercepted and returns to the atmosphere by evaporation, about 30% runs off the surface to enter streams, and about 60% of the precipitation enters the soil. However, of the water entering the soil by infiltration, the amount actually reaching the water table represents only about 2% of total precipitation, while transpiration returns the rest to the atmosphere (58% of total precipitation).

2.3 GROUND WATER–SURFACE WATER RELATIONSHIPS

Surface and near-surface ground water are intimately connected. Ground water that reaches the surface becomes surface water and vice versa. The direction(s) of flow between these two systems must be understood because contaminated ground water may contaminate surface water (ground water flows to the surface), or contaminated surface water may contaminate ground water (surface water flows to the ground).

2.3.1 Characteristics of Surface Water Flow

Channel storage refers to all of the water contained at any instant within the permanent stream channel. Runoff includes all of the water in a stream channel flowing past a cross section; this water may consist of precipitation that falls directly into the channel, surface runoff, ground-water runoff (also called *base flow*), and effluent. Stream flow, runoff, discharge, and yield of drainage basin are all nearly synonymous terms. Bank storage (Section 2.3.3) will also move into channel storage after flow in a stream channel drop from high-flow to intermediate and low-flow conditions.

Rates of flow are generally reported as cubic feet per second (cfs); millions of gallons per day (mgd); acre-feet per day, month, or year; cubic feet per second per square mile of drainage basin (cfs/mi²); or inches depth on drainage basin per day, month, or year. In the U.S., the most common unit of measurement for rate of flow is cubic feet per second.

Surface water discharge (Q) is determined by measuring the cross-sectional area of the channel (A), in square feet, and the average velocity of the water (v), in feet per second, so that

$$Q = Av \quad (2.2)$$

The cross-sectional area generally shows little change with time, so velocity is the main variable that must be measured to calculate stream flow. Typically, stream flow is measured by developing rating curves, in which accurate discharge measurements are made at low, intermediate, and high flows, and plotted against a gauge that measures the height of the stream at each discharge measurement. Once the rating curve has been fitted to the initial measurements, the flow at any gauge height can be estimated (provided that the channel geometry remains stable).

Surface water flow generally shows short-term fluctuations in response to individual precipitation events, and longer-term seasonal fluctuations. *Stream hydrographs* (plots of discharge as a function of time) are a useful way of viewing these fluctuations. Figure 2.3 shows a hydrograph in which individual peaks represent stream flow response to specific precipitation events. Seasonal fluctuations are also evident in this hydrograph, with lowest flow occurring in the fall. Another useful way to describe stream flow is the *flow-duration curve*, which shows the percentage of time discharge for the period of record equaled or exceeded various rates of discharge. *Base flow* (labeled as ground-water runoff in Figure 2.3) is the contribution of ground-water flow to a stream after all other contributions to stream flow have been subtracted out. Figure 2.3 shows that base flow fluctuates seasonally with a maximum in the spring and a minimum in the fall.

2.3.2 Drainage Basins

The drainage basin or *watershed* is the basic geographic unit for studying surface water. The watershed is the area that contributes water to a particular channel or set of channels. When the ground surface is saturated or precipitation exceeds the infiltration rate, surface runoff moves downhill until it reaches a stream. When several streams come together, the flows from their separate watersheds combine to form a larger watershed. Surface drainage basins are readily defined by topographic maps on which *drainage divides* mark the boundaries between watersheds.

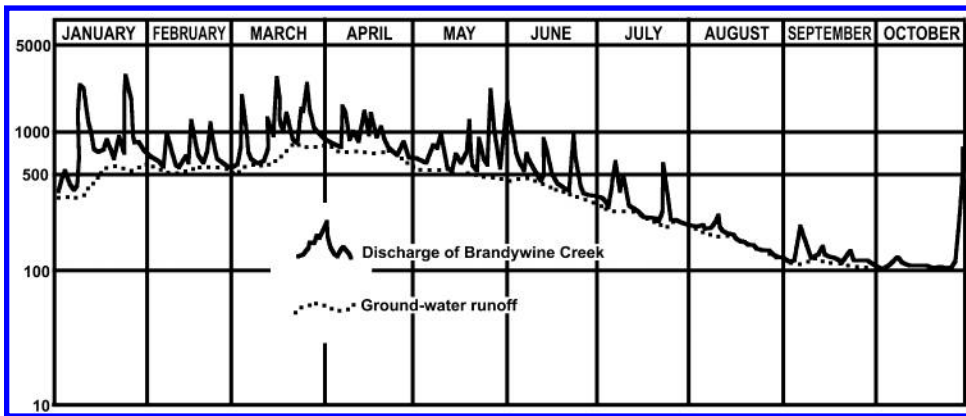


Figure 2.3 Hydrograph of Brandywine Creek, Chadd's Ford, PA, 1952–1953 (U.S. EPA, 1987a, after Olmsted and Hely, 1962).

Surface drainage patterns can be classified according to type of pattern and density. [Figure 2.4a](#) illustrates six basic drainage patterns, and [Figure 2.4b](#) shows coarse, medium, and fine densities. Stream segments can also be classified according to the number of tributaries. *First-order* streams have no tributaries and tend to be located in the upper reaches of a watershed. *Second-order* streams have as tributaries only first-order channels, *third-order* streams receive as tributaries only first- and second-order channels, and so on. [Figure 2.4b](#) shows stream orders for the coarse drainage density. Preliminary interpretation concerning geology and hydrogeology can be made by examining drainage patterns on aerial photographs or topographic maps. [Table 2.1](#) summarizes preliminary geologic and hydrogeologic interpretations that can be made based on drainage patterns illustrated in [Figure 2.4a](#).

Surface and ground-water drainage basins commonly coincide, but a perfect match should never be assumed. Situations where near-surface ground water and surface water watersheds may not include:

- Karst limestone terrane where subsurface drainage may have developed independently of surface drainage
- Sedimentary formations where the regional dip is in the opposite direction of surface water flow
- Areas where pumping of ground water has created disturbed normal ground-water flow patterns
- Areas where underground mining has altered subsurface flow patterns
- Heterogeneities in the subsurface near drainage divides, which may result in ground-water divides that differ from the topographic divide

2.3.3 Stream Types

From a hydrogeologic point of view, there are three major stream types: ephemeral, intermittent, and perennial. Stream type is determined by the relation between the water table and the stream channel.

An *ephemeral* stream owes its entire flow to surface runoff. It may have no well-defined channel, and the water table consistently remains below the bottom of the channel ([Figure 2.5, A-A'](#)). Water leaks from the channel into the ground, recharging the underlying strata.

Intermittent streams flow only part of the year, generally from spring to midsummer, as well as during wet periods. During dry weather, these streams flow only because of ground water that discharges into them when the water table rises above the base of the channel ([Figure 2.5, B-B'](#)). Eventually sufficient ground water discharges throughout the basin to lower the water table below the channel, which then becomes dry. This reflects a decrease in the quantity of ground water in

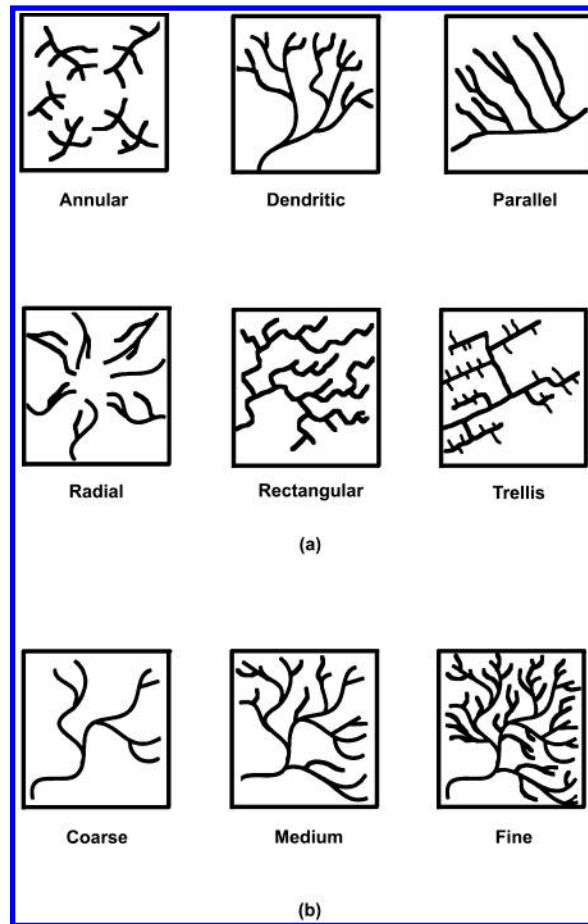


Figure 2.4 Drainage patterns: (a) six basic patterns; (b) drainage density variations (Kolm, 1993, after Way, 1973).

storage. During late summer or fall, a wet period may temporarily raise the water table enough for ground water to again discharge into the stream. Thus, during part of the year the floodplain materials are full to overflowing, causing the discharge to increase in a downstream direction; at other times, water will leak into the ground, reducing the discharge.

Perennial streams flow year-round. Typically, the water table is always above the stream bottom; hence, ground water is discharged to the surface, and stream flow increases downstream (Figure 2.5, C-C'). A stream in which the discharge increases downstream is called a *gaining stream*. When the discharge of a stream decreases downstream due to leakage, it is called a *losing stream*. In a losing stream, the water table is below the bottom of the stream, but the amount discharged to the subsurface is not enough to eliminate surface flow during periods of low flow. During wet periods, surface flow in perennial streams comes from a mixture of surface runoff and ground-water inflow. During dry periods, the flow of perennial streams comes primarily from ground-water discharge, and is called the *base flow*. Figure 2.3 shows the ground-water base flow component of Brandywine Creek. In this figure most of the flow in the months of August through October is ground-water base flow.

Normally, ground water flows into a gaining stream. However, short-term reversals in the direction of flow may occur in response to precipitation events. When the crest of runoff from a precipitation event passes a particular stream cross section, the stream level may rise higher than the water table, resulting in stream flow into the unsaturated portion of the stream bank. This

Table 2.1 Drainage Network Patterns as Indicators of Geologic/Hydrogeologic Systems

Drainage Pattern	Geologic/Geomorphic Indicator	Hydrogeologic Indicator
Annular	Structural and lithologic control; dome (alternating tilted stratified units; volcanic or sedimentary units) or caldera features; low or high slope gradients	Local flow systems prevail; sedimentary or volcanic hydrology; local and regional recharge areas; fracture and matrix flow
Dendritic	Lithologic control; flat-lying volcanic or sedimentary units; low slope gradient	Extensive regional and local flow systems possible; controlled by degree of topographic/geologic continuity; uniform lithology; matrix flow dominates
Parallel/subparallel	Structural or lithologic control; surficial units; slope control	Local flow systems prevail in surficial materials; matrix flow dominates
Radial	Structural and lithologic control; dome structures (intrusive), volcanic structures, erosional remnants; volcanic, crystalline, or sedimentary units; low and high slope gradients	Edges of regional flow systems; local flow systems prevail; local and regional recharge areas; fracture flow dominates if structural, mixed fracture and matrix flow dominate if volcanic, matrix flow dominates if erosional features
Rectangular	Structural control; uniform crystalline units (granite, carbonate, and volcanic rocks)	Regional (karst) and local (karst or igneous/metamorphic/sedimentary units) flow systems possible; fault and fracture zones control flow systems and location of discharge areas
Trellis	Structural and lithologic control; alternating tilted stratified units; volcanic or sedimentary units; low and high slope gradients	Local flow systems prevail; alternating aquifers and confining units; matrix and fracture flow possible

Source: Adapted from Kolm (1993).

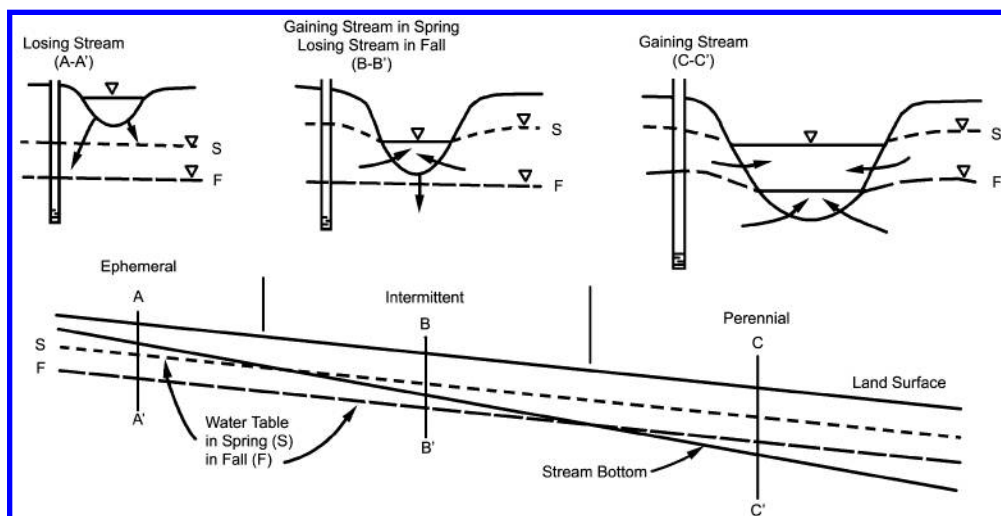


Figure 2.5 Relation between water table and stream type (U.S. EPA, 1987a).

occurrence blocks the ground water that would normally flow into the stream and causes the water table in the floodplain to rise. Once the stream begins to fall, the water that was recently added to the ground water will begin to flow back into the stream, rapidly at first and then more slowly as the water table gradient declines. This temporary storage of water in the near vicinity of the stream channel is called *bank storage* (Figure 2.6).

Nearly all water courses have headwater regions characterized by ephemeral streams. Farther downbasin, intermittent streams predominate, and even farther, the water courses are perennial. Some streams fed by springs or glacial meltwater are perennial throughout their entire length. The

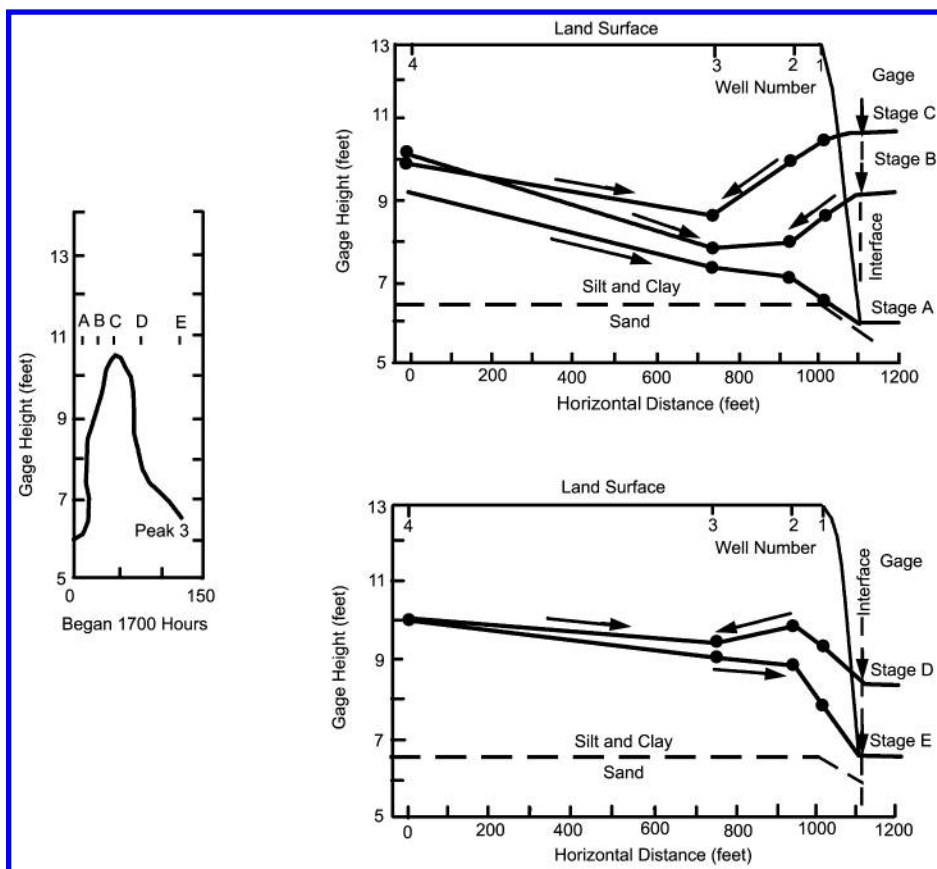


Figure 2.6 Movement of water into and out of bank storage along a stream in Indiana (Daniels et al., 1970).

natural gradation from one stream type to another may be interrupted by either natural or man-made causes. Irrigation may provide enough recharge to raise the water table sufficiently to increase ground-water runoff, while pumping from wells may have the opposite effect.

Streams flowing through saturated permeable deposits, such as sand and gravel, are normally gaining streams, but streams flowing through karst regions, or areas of extensive underground mining, may be losing in one reach and gaining in another. High dry-weather flow may reflect the discharge of water from mine workings.

2.3.4 Surface Water Quality

Under *base flow* conditions (i.e., stream flow comes entirely from ground-water discharge into the stream channel), the chemical quality of water in a perennial stream reflects the quality of ground water in the zone of active circulation within the basin, provided the stream is not contaminated by some surface source. During wet weather, the chemical quality of water in a stream varies largely because of the mixing of dilute surface runoff with the more highly mineralized ground-water runoff. The sediment load, reflecting erosion in the basin and stream channel, also affects the quality of the stream. The loading of a stream with either sediment or dissolved constituents is commonly reported in units of tons per day: short tons per day = discharge \times concentration \times 0.0027.²

² U.S. Environmental Protection Agency (EPA). 1987a. Handbook: Ground Water. EPA/625/6-87/016, 212 pp.

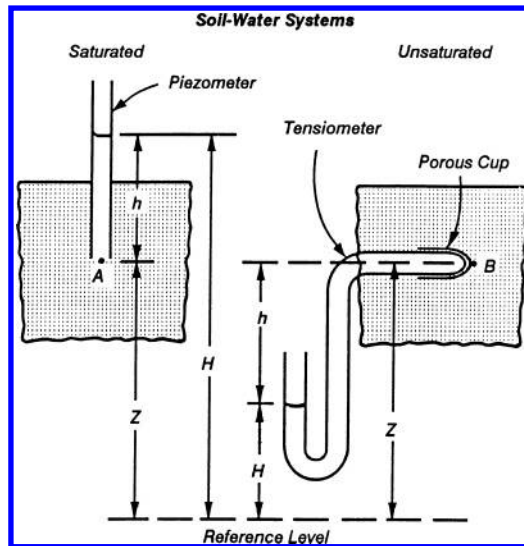


Figure 2.7 Diagram of the relationship between hydraulic head, H , pressure head, h , and gravitational head, z (Mercer and Spalding, 1991c).

2.4 WATER IN THE VADOSE ZONE

Historically, hydrogeologists have focused their attention on the *phreatic* (saturated) zone without paying much attention to water moving through the *vadose* (unsaturated) zone. The vadose cannot be ignored in the study of contaminant hydrogeology because it may be a significant reservoir for the capture, storage, and release of contaminants. Unsaturated fluid flow is complicated by matric and osmotic energy potentials (Section 2.4.1). Although the term *unsaturated zone* is often used loosely to refer to the vadose zone, part or all of this zone may be intermittently saturated and may contain several important subdivisions (Section 2.4.2).

2.4.1 Soil Water Energy Concepts

The retention and movement of water in the subsurface are energy-related phenomena. *Free energy* is the general term used to characterize the energy status of water. Water will tend to move or change from a higher to a lower free energy level, with the critical factor being differences in energy levels from one contiguous site to another.

Free energy of soil water is influenced by three major types of energy potentials:

- **Matric potential (P_m)** is the attraction of water to solids in the subsurface. Matric potential arises from both adsorption of water onto solids and capillary action in soil pores. The forces causing this energy potential *reduce* the free energy of water and are often called *matric suction* (see Figure 2.7). Generally, the smaller the particle and pore size, the greater the matric potential.
- **Osmotic potential (P_o)** results from dissolved constituents in subsurface water. The attraction of solute ions to water molecules reduces the free energy of water. Consequently, pure water will move across a semipermeable membrane to the side with a higher solute concentration. This is sometimes called *osmotic suction*. The higher the solute concentration differential across a membrane, the greater the osmotic suction. The negative pressure potential shown in Figure 2.7 represents the combined matric and osmotic suction.
- **Gravitational potential (P_g)** is the attraction of the force of gravity toward the earth's center. $P_g = Gh$, where G is the acceleration of gravity and h is height above a reference elevation (usually

chosen below the lowest point at which this potential will be measured so that the gravitational potential will always be positive).

Total soil water potential is the sum of the contributions of the various forces acting on soil water:

$$P_t = P_g + P_m + P_o + \dots \quad (2.3)$$

where the gravitational, matric, and osmotic potentials are as defined above and other less significant potentials are indicated by ellipses. Since gravity is a positive potential and matric and osmotic potentials are negative, water will only move through the soil profile if $P_g > P_m + P_o$. Various units of pressure are used to express soil water potential, the most common ones being 1 bar = 100 kilopascals (kPa) = 0.99 atmospheres (atm) = 1017 cm of water (H₂O). As discussed below, matric and osmotic potentials are significant forces affecting the movement of water in the unsaturated zone. In the saturated zone, gravitational potential is the dominant force.

2.4.2 Subdivisions of the Vadose Zone

The vadose zone has three major subdivisions (see Figure 2.8):

- *Soil water or root zone.* This zone lies between the ground surface and the maximum depth to which roots penetrate. It is characterized by large fluctuations in the quantity and quality of moisture in response to transpiration and evaporation. The rooting zone is commonly called the *soil water zone* in the hydrogeologic literature, but this term is not entirely accurate, since roots can penetrate well below the weathered zone of a soil profile. Local differences in gravitational, osmotic (created across root membranes), and matric potential will determine whether water entering the soil attaches to soil particles, is transpired by plants, or moves through the rooting zone.
- *Intermediate vadose.* This zone contains a residual moisture content determined by the matric potential. In coarse-grained material (sand and gravel), the amount of water held by matric potential is low; in fine-grained materials, particularly clays, the amount of water held may be very high. Since this zone also contains a significant amount of air in pore spaces, gravitational water reaching

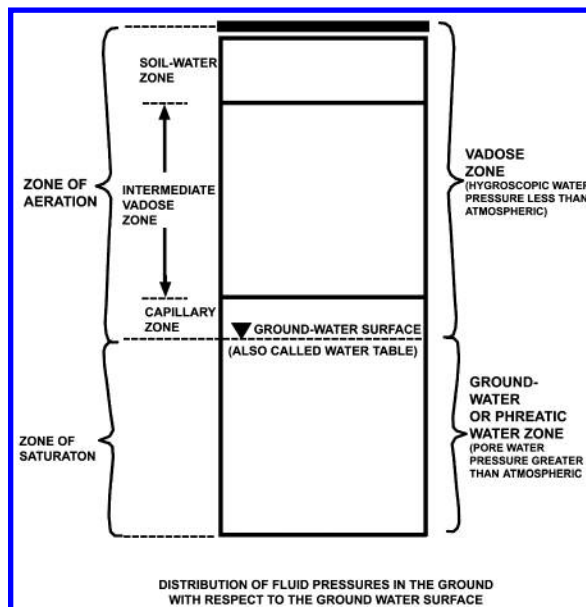


Figure 2.8 Classification of subsurface water (Sara, 1994).

this zone moves relatively slowly to the saturated zone by unsaturated flow until it reaches the capillary fringe.

- **Capillary fringe.** This zone marks the final transition between the vadose zone and the saturated zone. Capillarity is due to (1) the attractive forces of water solids, and (2) the surface tension of water. For water, the height of capillary rise in a tube can be calculated by the expression $h = 0.15/r$, where r is the radius of the tube. In other words, the smaller the diameter, the greater the capillary rise. Depending on the texture of the soil or geologic materials, this fringe may range from around 1 ft (sand) to 3 ft or more (loam).

Contaminants entering the vadose zone will tend to move more slowly than in the saturated zone because of the processes described above that retard the rate of water movement. For example, in the rooting zone, contaminants may be removed from the soil and incorporated into plant tissue, or they may remain in the soil after water is removed by transpiration until more water enters the soil and moves them farther down the soil profile.

2.4.3 Soil Moisture Retention Relationships

Matric suction in unsaturated soils, also called soil moisture tension, varies as a function of soil moisture content. A graphic plot of the relationship between soil moisture tension and volumetric water content may be referred to by a variety of names: *moisture retention*, *soil water retention*, *specific retention*, *moisture characteristic*, *specific moisture capacity*. Figure 2.9a shows moisture retention curves for USDA soil textures ranging from clay to sand. When soil moisture tension is zero, the soil is saturated or near saturation, and the volumetric water content is effectively equal to the porosity. As soil water content decreases, soil moisture tension increases. Figure 2.9a illustrates the significant effect that texture has on the moisture retention capacity. The volumetric water-holding capacity of sand at saturation is 43%, whereas at 100 mbar it is only about 5%. In

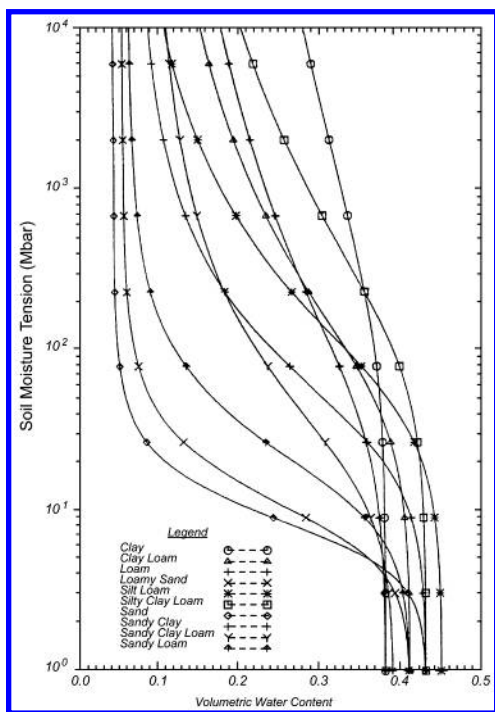


Figure 2.9a Moisture retention curves for various USDA soil textures (adapted from Mercer and Spalding, 1991d).

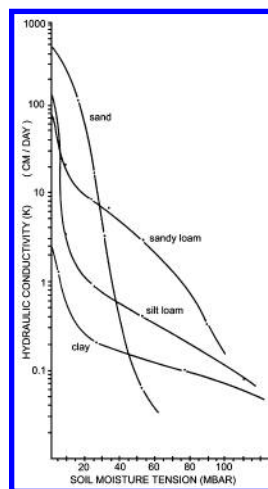


Figure 2.9b Relationship between hydraulic conductivity and soil moisture tension for various soil textures (Bouma et al., 1972).

contrast, the clay has a somewhat lower saturated water-holding capacity (38%), but is still holding about 28% water at 10,000 mbar of tension.

The generalized moisture retention curves shown in [Figure 2.9a](#) are useful for developing an understanding of how soil texture affects these relationships. However, it must be understood that a single texture class will have a range of curves and that they will be affected by other soil properties, such as porosity. Furthermore, moisture retention curves for a given soil sample will differ depending on whether measurements are made when the soil is wetting or drying. This effect is called *hysteresis*. Direct measurement of moisture retention curves is time-consuming, and a number of empirical equations have been developed to construct these curves based on correlations with soil physical properties such as sand and clay percentages and porosity. The Brooks–Corey and van Genuchten equations are two of the most commonly used empirical equations for estimating soil moisture retention curves and unsaturated hydraulic conductivity.³ Rawls et al. (1992)⁴ provide an excellent review of these and other equations and give empirical equations for estimating the Brooks–Corey parameters for pore-size index, bubbling pressure, and residual water from grain-size fractions and porosity.

2.4.4 Saturated vs. Unsaturated Flow

Saturated flow will occur in the vadose zone when the amount of water moving into the ground is sufficient to fill all the pore space in a soil. This is usually a temporary state because as soon as water stops flowing into the ground, gravitational water will flow relatively quickly into channels and the larger pore spaces in the soil. Usually gravitational water (where $P_g > P_m + P_o$) drains from the soil within 1 to 3 days. At this time, the soil is holding its *field capacity* of water, with approximately one half of the pore space filled with air and one half with water (moisture tension of about 100 mbar). A sandy soil has a low field capacity of about 1 in./ft of soil in the plant root zone that is reached quickly; clay-rich soils are characterized by high field capacities (3.5 to 4 in./ft) that are reached slowly. Fifteen bars (15,000 mbar) is the *wilting point* at which plants are no longer able to effectively remove moisture from the soil.

Water can flow by gravity through the soil even when it is not saturated. However, *rates* of unsaturated flow are substantially slower than rates of saturated flow. [Figure 2.9b](#) shows that *hydraulic conductivity* (the rate of flow in centimeters/day) of the clay at saturation (at or near zero matric suction) is about 10 times higher than at a matric suction of 60 mbar. In contrast, the hydraulic conductivity of the sand increases about four orders of magnitude over the same moisture tension range. [Figure 2.9b](#) also illustrates that the *saturated* hydraulic conductivity of the sand is about two orders of magnitude higher than that of clay soil. The relationship reverses under unsaturated conditions, such that the *unsaturated* hydraulic conductivity of the sand is *lower* than that of the clay soil when soil moisture tension is greater than about 45 mbar. These variations, plus variations in texture and pore-size distribution in the vadose zone, make moisture status and movement difficult to measure.

Saturated flow in the vadose zone takes place at or near zero suction, and Darcy's law for calculating water flow applies ([Section 2.6.3](#)). For steady unsaturated flow (such as when a continuous source of water is applied to the soil at a rate that is below the saturated hydraulic conductivity), Buckingham (1907)⁵ developed a modified form of Darcy's equation. A much more common situation is for water flow to be transient; that is, the water content and soil moisture tension vary with time. This more complicated situation requires a nonlinear partial differential

³ Brooks, R.J. and A.T. Corey. 1964. Hydraulic Properties of Porous Media. Hydrology Paper 3, Colorado State University, Fort Collins, CO, 27 pp.

van Genuchten, M.Th. 1980. Predicting the Hydraulic Conductivity of Unsaturated Soils. Soil Science Society of America Journal 44:892–898.

⁴ Rawls, W.J., L.R. Ahuja, and D.L. Brakensiek. 1992. Estimating soil hydraulic properties from soils data, in *Indirect Methods for Estimating the Hydraulic Properties of Soils*, M.Th. van Genuchten, F.J. Leij, and L.J. Lund, Eds., University of California, Riverside, CA, pp. 329–340.

⁵ Buckingham, E. 1907. Studies on the Movement of Soil Moisture. U.S. Department of Agriculture Bull. 18.

equation developed by Richards (1931).⁶ Nonlinear equations are difficult to solve analytically, so Richard's equation is usually solved numerically using computer codes, although approximate analytical solutions have been developed as described by Hogarth and Parlange (2000).⁷

2.5 WATER IN THE SATURATED ZONE (1): FUNDAMENTAL CONCEPTS

2.5.1 Hydraulic Head and Gradients

The water level in a well, usually expressed as feet above sea level, is the total head (h_t), which consists of elevation head (z) and pressure head (h_p) — see [Figure 2.7](#).

$$h_t = z + h_p \quad (2.4)$$

In an unconfined aquifer, pressure head (h_p) equals zero at the water table surface because it marks the transition from negative pressure head in the vadose zone to a pressure head that may be either negative or positive in the saturated zone. Serious inaccuracies in defining ground-water flow paths may result from measuring water levels in monitoring wells without considering the pressure potential component (Section 7.2).

In a ground water *recharge* zone, the pressure head *decreases* with increasing depth (i.e., h_p in Equation 2.4 is negative); in a *discharge* zone, the pressure head *increases* with depth. This is illustrated in [Figure 2.10](#). In the figure, the water level in piezometer c is the same as that in well b since it lies along the same equipotential line. The water level in well b is lower than the water table surface at that well location. This is because the well is cased to a depth where it is actually measuring the pressure potential of the water table at well c. Conversely, wells d and e in the discharge area are measuring the pressure potential of the water table upslope from the actual discharge area. Wells d and e will flow like artesian wells even though there is no confining layer.

Typically, wells are not installed at different depths in the same location to allow determination of whether the area is in a recharge or discharge zone. Topography is a simple indicator, with discharge in topographically low areas and recharge in topographically high areas.

The hydraulic gradient (I or i) is measured as the change in water level per unit of distance along the direction of maximum head decrease. It is determined by measuring the water level in several wells that measure the true unconfined water table or the same confined aquifer. The hydraulic gradient is the driving force that causes ground water to move in the direction of decreasing total head, and is generally expressed in consistent units such as feet per foot. For example, if the difference in water level in two wells 1000 ft apart is 8 ft, the gradient is 8/1000 or 0.008. The direction of ground water movement and the hydraulic gradient can be determined with information from three wells (Section 7.2.2).

2.5.2 Unconfined and Confined Aquifers

Aquifers are broadly classified as *unconfined*, where the top of the saturated zone is at atmospheric pressure, and *confined*, where a slowly permeable geologic layer prevents upward flow when the hydraulic head is above the level of the confining layer, causing pressure head at the top of the aquifer to exceed atmospheric pressure. Confining layers or units may also be called *aquitards* or *aquicludes* in the older literature. Confined aquifers are classified as either *semiconfined* or *leaky* and *confined*, depending on how permeable the confining layer is. Because no confining unit is

⁶ Richards, L.W. 1931. Capillary Conduction of Liquids in Porous Mediums. *Physics* 1:318–333.

⁷ Hogarth, W.L. and J.Y. Parlange. 2000. Application and Improvement of a Recent Approximate Analytical Solution of Richard's Equation. *Water Resources Research* 36:1965–1968.

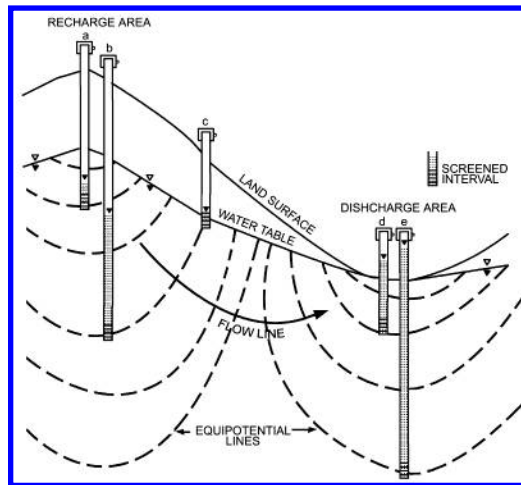


Figure 2.10 Cross-sectional diagram showing the water level as measured by piezometers located at various depths (Mills et al., 1985).

completely impermeable, Kreitler and Senger (1991)⁸ have suggested using the term *highly confined* for confining units with very low permeability. Section 7.5.3 identifies methods for characterizing presence and degree of confinement. Aquifer classification is especially important in selecting methods for interpreting pump test data and serves as an indicator of the vulnerability to ground-water contamination.

In humid and semiarid regions in particular, the water table in an unconfined aquifer generally conforms to the surface topography, although it usually has greater depth under hills than under valleys (Figure 2.10). The hydraulic gradient (Section 2.5.1) slopes away from divides and topographically high areas toward adjacent low areas, such as streams and rivers. The high areas serve as ground-water recharge areas, while the low areas are ground-water discharge zones. In general, the water table lies at depths ranging from 0 to about 20 ft in humid and semiarid regions, but often lies hundreds to thousands of feet deep in some desert environments. Generally, surface streams and waterbodies such as swamps, ponds, lakes, and flooded excavations (abandoned gravel pits, highway borrow pits, etc.) can be considered surface expressions of the water table.

Unconfined water tables may be either *perched* or *regional*. Perched water tables rest on impermeable strata, below which unsaturated flow occurs (see Figure 2.11, upper right corner). In regional aquifers, all water moves by saturated flow until it reaches a point of surface discharge (Figure 2.11, Aquifer C). Aquifers A and B in Figure 2.11 exhibit characteristics of both perched and regional water tables. Most of their water is part of the regional water, although it may travel partway by unsaturated flow before reaching Aquifer C. Some water, however, reaches the surface as springs, a common situation with perched aquifers.

2.5.3 Heterogeneity and Anisotropy

Aquifers in which the hydraulic conductivity or other properties are nearly uniform are called *homogeneous*; those in which properties are variable are *heterogeneous* or nonhomogeneous. If hydraulic conductivity at a given point in an aquifer differs in the vertical or horizontal directions, it is *anisotropic*. If hydraulic conductivity is uniform in all directions, which is rare, the aquifer is *isotropic*. Figure 2.12a illustrates four possible combinations of these characteristics. The distinctions between these terms may not seem obvious at first, but a careful examination of this figure should provide a clearer understanding.

⁸ Kreitler, C.W. and R.K. Senger. 1991. Wellhead Protection Strategies for Confined-Aquifer Settings. EPA/570/9-91-008, 168 pp.

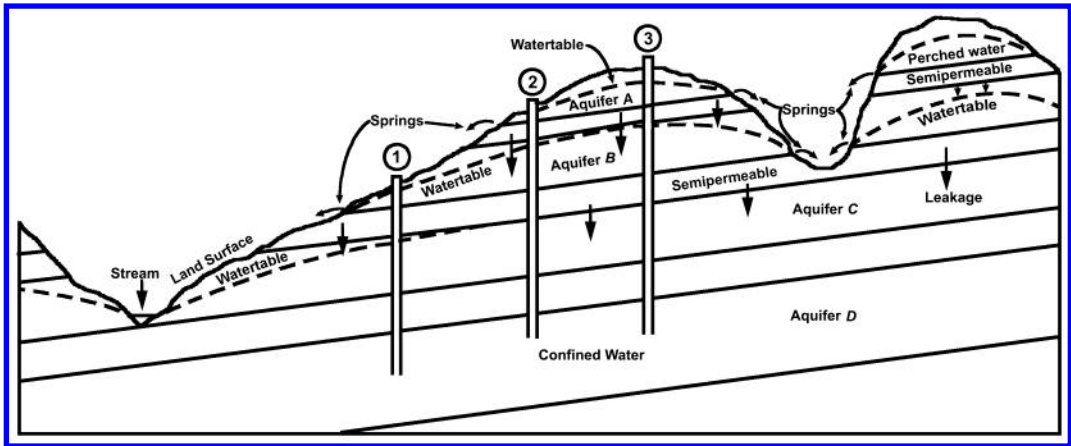


Figure 2.11 Confined, unconfined, and perched water in a simple stratigraphic section of sandstone and shale (Davis and DeWiest, 1966).

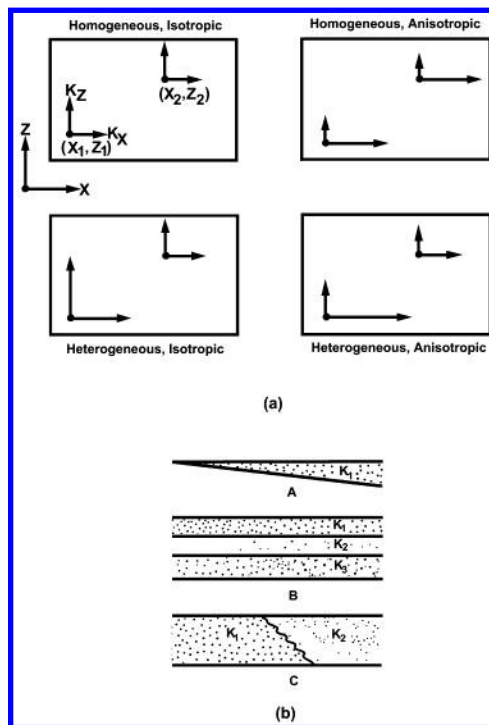


Figure 2.12 Heterogeneity and anisotropy: (a) four possible combinations (Physical Properties and Principles, Chapter 2 in Groundwater, Freeze/Cherry © 1979, reprinted by permission of Prentice Hall, Englewood Cliffs, NJ); (b) three types of aquifer heterogeneity (adapted from Fetter, 1994).

Figure 2.12b illustrates three different types of aquifer heterogeneity: (1) varying thickness (A, common with fluvial and deltaic sediments), (2) layering with different hydraulic conductivities (B, common with sediments deposited under water bodies), and (3) lateral changes in hydraulic conductivity (C, common with glaciofluvial deposits and areas of complex geologic structure). Because both unconsolidated and consolidated sedimentary strata are typically deposited in horizontal units (example B in the figure), hydraulic conductivity is generally greater horizontally than vertically by at least an order of magnitude. The third example (C in the figure) is most likely to

occur as a result of faulting or other tectonic activity. Failure to consider heterogeneity and anisotropy can lead to significant underestimation of time of travel of contaminants and incorrect delineation of the direction of ground-water flow.

2.5.4 Porous Media vs. Fracture/Conduit Flow

Ground water flows in the interconnected pore spaces between solid particles in an aquifer. Most ground-water flow equations assume that the water is flowing through material where the pore sizes are small enough that water flows without turbulence. This is generally true in aquifers where *primary* or *matrix porosity* has not been altered by geologic or soil-forming processes that create secondary openings, often called *secondary porosity*. Secondary openings are classified as *fractures*, which develop as a result of deformation and stress release by geologic processes, and *solution* openings, which are formed from the enlargement of fractures by dissolution of soluble minerals such as carbonate in limestone.

Flow in fractures is most significant in crystalline rocks (granites, various metamorphic rocks) because primary porosity of these rocks is very low. Many consolidated sedimentary aquifers are fractured to varying degrees. Aquifers where fracture flow is significant tend to be anisotropic. Ground-water flow directions in these aquifers may depart significantly from the directions indicated by potentiometric surface maps. Analysis of aquifer test data in fractured rocks requires special care because most analytical solutions assume porous media flow (Section 7.5.4). However, fractures are typically narrow enough to prevent turbulent flow, making adaptation of ground-water flow equations possible. Fracture flow is a major contributor to macroscale hydrodynamic dispersion, causing contaminants to move much more quickly in an aquifer than would be predicted by flow calculations based on primary porosity.

Flow in cavernous limestones and dolomites is called *conduit* flow. The subsurface channels can be large and continuous enough that the system is more like a series of interconnected pipes than a porous material. As with crystalline rocks, primary porosity of limestones tends to be very low, so that most ground-water flow is concentrated in fractures and solution channels. Aquifers where conduit flow dominates are called *karst* aquifers. However, unlike fractured rock aquifers, ground-water flow in karst aquifers is often rapid enough that Darcy's law (Section 2.6.3) is not valid (Section 7.5.4). The irregular shape of solution channels in these aquifers makes the use of conventional methods for analyzing pump test data and modeling ground-water flow essentially useless. Figure 1.9 illustrates the wide fluctuation in ground-water levels that can occur in a karst aquifer. Table 1.4 identifies major references where more information can be obtained about karst geomorphology and hydrology.

2.5.5 Ground Water Fluctuations

Ground-water levels fluctuate throughout the year in response to natural changes in recharge and discharge (or storage), changes in pressure, and artificial stresses. Fluctuations brought about by changes in pressure are limited to confined aquifers. Most of these changes are short term and are caused by loading, such as by a passing train compressing the aquifer, or by an increase in discharge from an overlying stream. Others are related to changes in barometric pressure, tides, and earthquakes. Languth and Treskatis (1989)⁹ describe an unusual situation where an aquifer test in a semiconfined aquifer system temporarily increased water levels in observation wells tapping the overlying confining bed, instead of resulting in the usual immediate lowering. None of these fluctuations reflects a change in the volume of water in storage. Table 2.2 summarizes 13 mechanisms that lead to fluctuations in ground water levels.

⁹Languth, H.R. and C. Treskatis. 1989. Reverse water level fluctuations in semiconfined aquifer systems — “Rhade Effect”, *J. Hydrology*, 109, 79–93.

Table 2.2 Summary of Mechanisms That Lead to Fluctuations in Ground Water Levels

	Unconfined	Confined	Natural	Man Induced	Short Term	Diurnal	Seasonal	Long Term	Climatic
Ground-water recharge	x		x				x		x
Air entrapment during recharge	x		x		x				x
Evapotranspiration	x		x			x			x
Stream bank storage effects	x		x				x		x
Tidal effects near ocean	x	x	x			x			
Atmospheric pressure effects	x	x	x			x			x
Confined aquifer external loading		x		x	x				
Earthquakes		x	x		x				
Ground-water pumpage	x	x		x				x	
Deep-well injection		x		x				x	
Artificial recharge/leakage	x			x				x	
Agriculture irrigation/drainage	x			x				x	x
Geotechnical drainage	x			x				x	

Source: Adapted from Freeze and Cherry (1979).

Water level fluctuations in confined aquifers can be characterized by the *barometric efficiency*, the ratio of change in head to change in atmospheric pressure. This ratio usually falls in the range of 0.20 to 0.75. The possibility of using barometric efficiency to estimate the storage properties of confined aquifers was first suggested by Jacob (1940).¹⁰ Barometric efficiency can be used to estimate a range of aquifer properties, including storage coefficient, transmissivity, and bulk elastic properties.¹¹

Fluctuations that involve changes in storage are generally more long-lived. Most ground-water recharge takes place during the spring and causes the water level to rise. Following this period of a month or two, the water level declines in response to natural discharge, largely to streams. Although the major period of recharge occurs in the spring, minor events can happen any time it rains. A number of human activities cause long-term fluctuations in ground-water levels. Ground-water pumpage reduces ground-water levels; activities such as agricultural irrigation, artificial recharge, and leakages from ponds, lagoons, and landfills tend to cause localized increases in ground-water levels. Deep-well injection into confined aquifers also causes elevation in the potentiometric surface.

Evapotranspiration effects on a surficial or shallow aquifer are both seasonal and daily. Plants, serving as minute pumps, remove water from the capillary fringe or even from beneath the water table during hours of daylight in the growing season. This results in a diurnal fluctuation in the water table and stream flow.

Table 2.3 summarizes typical natural conditions affecting ground-water fluctuations in response to (1) freezing, (2) moisture regime, (3) surface drainage and degree of slope, and (4) thickness of the zone of aeration. All these factors need to be considered in compiling data on water levels in wells when preparing potentiometric surface maps (Section 7.2).

2.5.6 Ground Water Divides and Other Aquifer Boundaries

In surface hydrology, a drainage divide forms the boundary between two watersheds. Ground-water drainage basins are similar to surface watersheds, except that they are defined by contours of equal hydraulic head (equipotential lines) rather than topographic contours. In unconfined, homogenous, isotropic aquifers, these contours generally follow the surface topography, albeit with a more subdued gradient (Figure 2.10 and Figure 2.11). However, topography is only one of many factors that influence the location of ground-water divides and the flow of water within a basin. An understanding of the *boundary conditions* in an aquifer is essential when mapping aquifers and when using ground-water computer models (Chapter 10).

Figure 2.11 illustrates several ground-water divides. Infiltrating water entering the aquifer at the recharge area flows to a discharge point determined by where the water table intersects the ground surface. Note that the topographic divide for Aquifer A does not quite coincide with the ground-water divide due to the dip of the sediments.

Figure 2.13 illustrates more than 40 boundary conditions that may define the edges of a ground-water drainage area. These boundary conditions are classified as (1) *barrier boundaries*, created by geologic or other materials of contrasting (lower) permeability compared to the aquifer, (2) *permeable recharge* boundaries, and (3) *permeable discharge* boundaries. Figure 2.13 further classifies boundary conditions according to whether they represent head conditions or flow conditions. It also shows the number of dimensions required to represent the condition: (1) points (one-dimensional), (2) lines (two-dimensional), and (3) areas (three-dimensional). These distinctions become important when analytical and numerical ground-water models are selected and used (Chapter 10). Where streams form boundaries to an aquifer, it is important to determine whether

¹⁰ Jacob, C.E. 1940. On the Flow of Water in an Elastic Artesian Aquifer. Transactions of the American Geophysical Union 21:574–586.

¹¹ Ritz, R.W., S. Sorooshian, and P.A. Hsieh. 1991. The Estimation of Fluid Flow Properties from the Response of Water Levels in Wells to the Combined Atmospheric and Earth Tide Forces. Water Resources Research 27(5):883–893.

Table 2.3 Factors and Natural Conditions Affecting Natural Ground Water Fluctuations

Factor/Zone	Ground Water Conditions and General Characteristics of Water Level Fluctuations
Soil Freezing	
1. Permafrost areas	Two summer water level rises.
2. Uniform freezing in the soil zone at the land surface	Marked water level rise in the spring, followed by water level recession until autumn. A second smaller water level rise in autumn, followed by gradual decline until spring. Aquifer may change from water table conditions during summer to confining conditions when the soil is frozen.
3. Sporadic freezing of the zone of aeration	Water level rises mainly in the winter.
4. Complete absence of soil freezing	Water level rises during rainy season.
Soil Moisture Regime	
1. Region of high moisture	The amount of precipitation is higher than evapotranspiration. Water levels affected rapidly by small rains and small temperature variations. Small amplitude of water fluctuations.
2. Region of moderate moisture	As water table is at greater depth than in zone 1, amplitudes of water level fluctuations are more distinct and greater than those in zones 1 and 3.
3. Region of small moisture	Evapotranspiration is a dominant factor in water level fluctuations.
Surface Drainage and Degree of Slope	
1. Well-developed drainage (generally mountainous topography)	High runoff and low infiltration to ground water. Water level fluctuation amplitude may be high.
2. Moderately developed drainage (generally uplands)	Moderate runoff and infiltration to ground water. Water level fluctuation amplitudes are lower than those in zone 1 but higher than those in zone 3.
3. Poorly developed drainage (generally plains and valley bottoms)	Low runoff and high infiltration to ground water. Water table at shallow depth. High evapotranspiration.
Thickness of Zone of Aeration (d)	
1. $d < 0.5$ m	Water level fluctuations of small amplitude. Evapotranspiration from the water table prevails over spring discharge.
2. $0.5 < d < 4$ m	Water level fluctuations of larger amplitude than in zone 1. Spring discharge prevails over evapotranspiration.
3. $d > 4$ m	Water level fluctuations of small amplitude and evapotranspiration might be of limited importance.

Source: Adapted from Brown et al. (1983).

they are *gaining* or *losing* streams ([Section 2.3.3](#)) to develop correct interpretations of the ground-water flow system.

2.6 WATER IN THE SATURATED ZONE (2): WATER STORAGE AND FLOW

Key questions that most ground-water studies must answer are (1) how much water is available from an aquifer, and (2) how fast is water moving through the aquifer? The answers to these questions require measurement or estimation of aquifer storage properties (porosity, and specific yield or storativity) and aquifer transmitting properties (hydraulic conductivity and transmissivity).

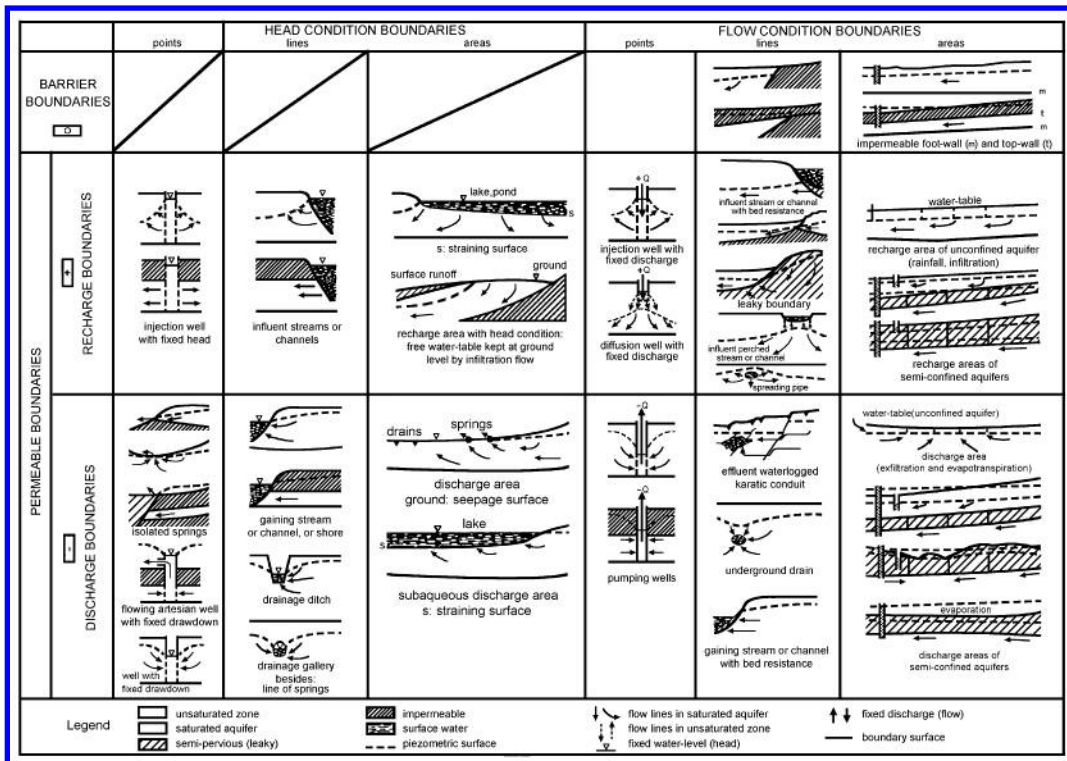


Figure 2.13 Types of aquifer boundary conditions (Struckmeier et al., 1986, after Castany and Margat, 1977).

2.6.1 Aquifer Storage Properties: Porosity and Specific Yield/Storativity

Porosity, expressed as a percentage or decimal fraction, is the ratio between the openings in the rock and the total rock volume. It defines the amount of water a saturated rock volume can store. If a unit volume of saturated rock drains by gravity, not all of the water it contains will be released. The volume drained is the *specific yield*, a percentage, and the volume retained is the *specific retention*. Therefore, porosity is equal to specific yield plus specific retention. Knowing any two of these terms allows calculation of the third.¹² Table C.1 and Table C.2 show some typical values for porosity and specific yield for various soil and geologic materials. Actual values for specific materials can differ substantially from the numbers shown here.

Another important term is *storativity* (*S*), which describes the quantity of water that an aquifer will release from storage or take into storage per unit of its surface area per unit change in head. In unconfined aquifers, the storativity is, for all practical purposes, equal to the *specific yield*. The storativity of confined aquifers is substantially smaller than specific yield (Table C.2), because the water released from storage when the head declines comes from the expansion of water and compression of the aquifer, both of which are very small. For confined aquifers, storativity generally ranges between 0.005 and 0.00005, with leaky confined aquifers falling in the high end of this range.¹³ The small storativity of confined aquifers means that a large pressure change throughout a wide area is needed to obtain a sufficient supply from a well. This is not the case with unconfined aquifers, because the water derived is not related to expansion and compression, but instead comes from gravity drainage and dewatering of the aquifer.

¹² This includes only interconnected pores through which water can flow. Isolated pores, whether air- or water-filled, can be considered part of the solid volume of a rock for purposes of ground-water flow analysis.

¹³ 0.0001 to 0.00001 may also be cited in the literature as a typical range.

2.6.2 Water-Transmitting Properties: Hydraulic Conductivity and Transmissivity

The terms *permeability* (P) and *hydraulic conductivity* (K) are often used interchangeably to refer to the ease with which water moves through soil or an aquifer under saturated conditions. Hydrogeologists draw a distinction between *intrinsic permeability* (k — a property of the porous medium alone that is independent of the nature of the liquid or potential field) and *hydraulic conductivity* (K — a function of both the medium and the fluid flowing through it). A precise definition of hydraulic conductivity is:

The quantity of water that will flow through a unit cross-sectional area of a porous material per unit of time under a hydraulic gradient of 1.0 (measured at right angles to the direction of flow) at a specified temperature.¹⁴

ASTM defines hydraulic conductivity measured from field aquifer tests as follows:

The volume of water at the existing kinematic viscosity that will move in a unit time under unit hydraulic gradient through a unit area measured at right angles to the direction of flow. (ASTM 4043/TA.14)

The terms *hydraulic conductivity* and *permeability* in this handbook refer to saturated hydraulic conductivity unless otherwise specified. Soil permeability rates are typically reported in units of inches per hour based on percolation tests. Hydraulic conductivity may be reported in a variety of units: $\mu\text{m}/\text{second}$, cm/second , m/second , ft/day , and gpd/ft^2 (gallons per day per square foot). Currently, centimeters per second is probably the most commonly used unit. Hydraulic conductivity values range widely from one rock type to another, and even within the same rock. Table C.3 and Figure C.3 through Figure C.15 identify ranges of hydraulic conductivity for a variety of soil and geologic materials.

Transmissivity (T), a term derived from hydraulic conductivity, describes the capacity of an aquifer to transmit water. Transmissivity is equal to the product of the aquifer's saturated thickness (b) and the hydraulic conductivity (K). It is commonly measured in units of gpd/ft of aquifer thickness:

$$T = Kb \quad (2.5)$$

2.6.3 Darcy's Law

Darcy's law, expressed in many different forms, allows calculation of the quantity of water flowing through a defined area of an aquifer, provided that the hydraulic conductivity and the hydraulic gradient are known. One means of expressing Darcy's law is

$$Q = KiA \quad (2.6)$$

where:

Q = quantity of flow per unit of time, in gpd

K = hydraulic conductivity, in gpd/ft^2

i = hydraulic gradient

A = cross-sectional area through which the flow moves, in ft^2

¹⁴From glossary in Nielsen, D.M. (ed.). 1991. Practical Handbook of Ground Water Monitoring. Lewis Publishers, Chelsea, MI, 717 pp.

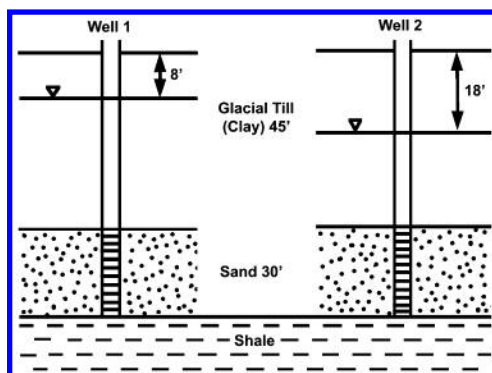


Figure 2.14 Using Darcy's law to estimate underflow in an aquifer (U.S. EPA, 1987a).

Darcy's law assumes that flow is *laminar*, which means that the water will follow distinct flow lines rather than mix with other flow lines. Most ground-water flow in porous media is laminar. The equation does not work for *turbulent* flow, as in the case of the unusually high velocity that might be found in fractures or solution openings or in granular aquifers adjacent to some pumping wells.

Figure 2.14 shows an example of the use of Darcy's law. In this case, a sand aquifer about 30 ft thick lies within the flood plain of a river about 1 mi wide. The aquifer is covered by a confining unit of glacial till, the bottom of which is about 45 ft below the land surface. The difference in water level in two wells 1 mi apart is 10 ft, and the hydraulic conductivity of the sand is 500 gpd/ft². Therefore, the quantity of underflow moving through the cross section in Figure 2.14 is

$$Q = KiA = 500 \text{ gpd/ft}^2 \times (10 \text{ ft}/5280 \text{ ft}) \times (5280 \times 30) = 150,000 \text{ gpd}$$

2.6.4 Flow Between Aquifers

To determine the flow from one aquifer to another via a confining unit, a slightly modified form of Darcy's law can be used:

$$Q_l = (p/m)A\Delta h \quad (2.7)$$

where:

Q_l = quantity of leakage, in gpd

p = vertical hydraulic conductivity of the confining unit, in gpd/ft²

m = thickness of the confining unit, in ft

A = cross-sectional area, in ft²

Δh = difference in head between the two wells

Figure 2.15 illustrates two aquifers separated by a layer of silt. The silty confining unit is 10 ft thick and has a vertical hydraulic conductivity of 2 gpd/ft². The difference in water level between wells tapping the upper and lower aquifers is 15 ft. Assuming these hydrogeologic conditions exist in an area of 1 square mi, the daily quantity leaking from the shallower aquifer to the deeper one within the area is

$$Q_l = (2 \text{ gpd/ft}^2/10 \text{ ft}) \times 5280^2 \times 15 \text{ ft} = 83,635,200 \text{ gpd}$$

This calculation clearly shows that the quantity of leakage, either upward or downward, can be highly significant even if the hydraulic conductivity of the confining unit is small.

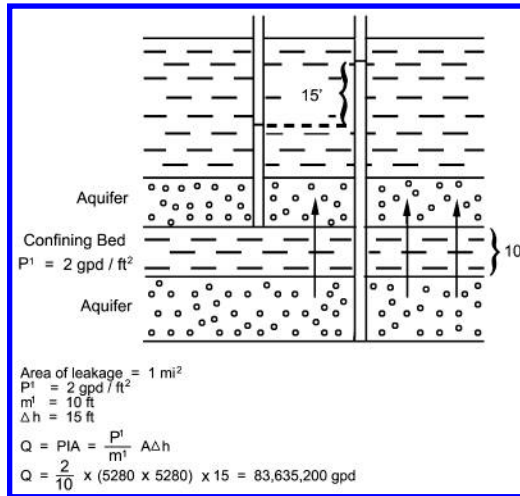


Figure 2.15 Using Darcy's law to calculate the quantity of leakage from one aquifer to another (U.S. EPA, 1987a).

2.6.5 Interstitial Velocity and Time of Travel

The time it takes ground water to travel a specified distance is particularly important in contamination studies. Time of travel can be estimated using the form of Darcy's law that describes average linear velocity:

$$\bar{v} = Ki/n \quad (2.8)$$

where:

\bar{v} = average interstitial (linear) velocity

K = horizontal hydraulic conductivity

i = horizontal hydraulic gradient

n = porosity

This equation is most easily used when a potentiometric map of the aquifer is available for measuring hydraulic gradients. For preliminary calculations, K and n can be estimated (see Appendix C). Once average velocity is known, the time of travel over a given distance can be easily calculated:

$$t = d/\bar{v} = dn/Ki \quad (2.9)$$

where:

t = time of travel

d = distance

Or the distance to time of travel contours is calculated as follows:

$$d = \bar{v}t = tKi/n \quad (2.10)$$

where terms are the same as described in Equation 2.8 and Equation 2.9. This equation is most applicable to the following situations:

- To calculate time of travel in a highly confined aquifer with a nearly flat potentiometric surface (gradient of <0.0005 to 0.001)

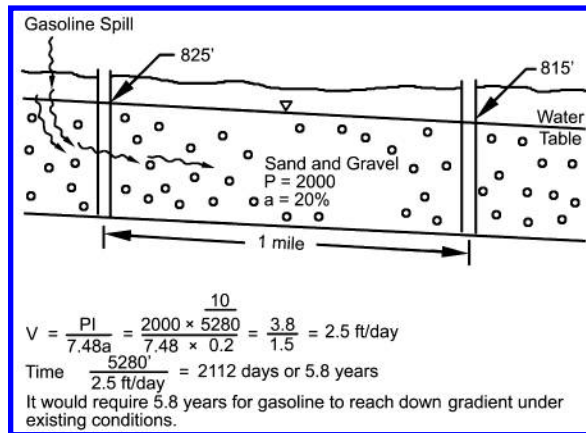


Figure 2.16 Ground water velocity calculations (U.S. EPA, 1987a).

- To calculate time of travel in an unconfined aquifer with a nearly flat water table and when drawdown is small compared to the aquifer thickness or screened interval (<10%)
- To calculate time of travel of a contaminant from a point source to a downgradient point of interest, *if* the equipotential lines are approximately equally spaced between the two points (i.e., the aquifer is homogeneous)

Somewhat more complex methods are required for wells with steep gradients in the cone of depression and wells in areas where there is a sloping regional water table.

The following example involves a spill of a conservative substance such as chloride. The liquid waste infiltrates through the unsaturated zone and quickly reaches an unconfined aquifer that consists of sand and gravel with a hydraulic conductivity of 2000 gpd/ft² and an effective porosity of 0.20. The water level in a well at the spill lies at an altitude of 1525 ft and, at a well a mile directly downgradient, is at 1515 ft (Figure 2.16). The velocity of the water and the contaminant and the time it will take for the chloride to contaminate the second well can be determined by the following equations:

$$v = (2000 \text{ gpd/ft}^2) \times (10 \text{ ft}/5280 \text{ ft}) / 7.48 \times 0.20 = 2.5 \text{ ft/d}$$

$$\text{Time} = 5280 \text{ ft} / 2.5 \text{ ft/d} = 2112 \text{ days or 5.8 years}$$

This velocity value is crude at best and can only be used as an estimate. For example, the equation does not consider hydrodynamic dispersion (see Section 4.4.2). Velocity of most chemical species is further affected by reactions with the geologic framework, particularly with certain clays, soil-organic matter, and certain hydroxides (Section 4.5). Only conservative substances such as the chloride ion will move unaffected by retardation. See Section 4.5.3 for the equation to calculate the retardation factor when sorption is linear.

In addition, not only the water below the water table is moving, but also fluids within the capillary fringe. There the velocity diminishes rapidly upward from the water table. Movement in the capillary fringe is important where the contaminant is gasoline or another substance less dense than water.

2.6.6 Ground-Water Pumping Concepts

Cone of Depression. When a well is pumped, the water level declines to provide a gradient that drives water toward the discharge point. The gradient becomes steeper closer to the well,

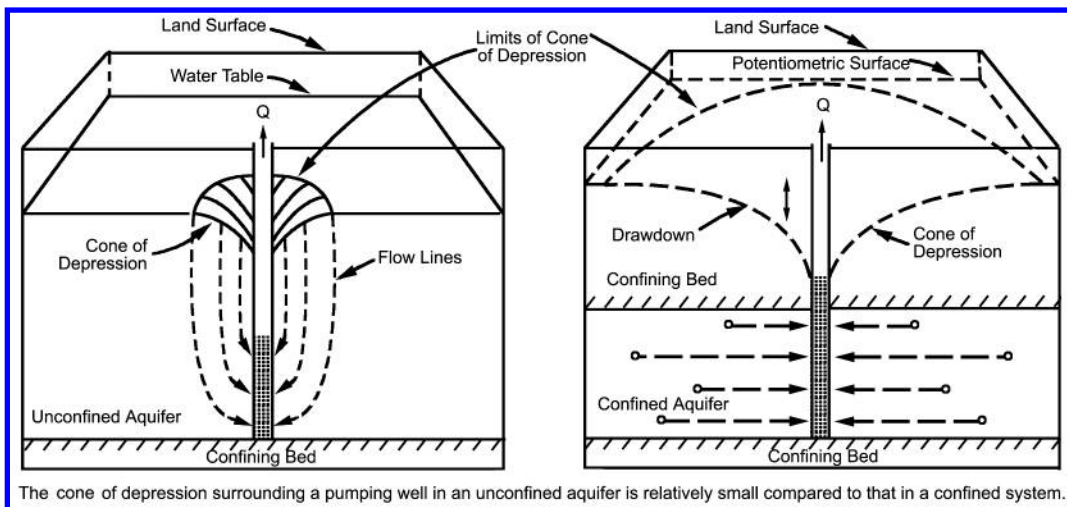


Figure 2.17 Cones of depression in unconfined and confined aquifers (Heath, 1983).

because the flow is converging from all directions, and the area through which the water flows gets smaller. This results in a cone of depression around the well (Figure 2.17). The cone of depression around a well tapping an unconfined aquifer is relatively small compared to that around a well in a confined system because more water is released per foot of drawdown. In a confined aquifer the release of pressure with pumping moves very quickly through the aquifer, whereas water moves more slowly. The cone of depression of unconfined aquifers may be tens to a few hundred feet in diameter, while in confined aquifers it may extend outward for miles.

Cones of depression from several pumping wells may overlap, and since their drawdown effects are additive, the water level decline throughout the area of influence is greater than that from a single cone. In ground-water studies, particularly of contamination problems, evaluation of the cone or cones of depression can be critical; they represent an increase in the hydraulic gradient, which controls ground-water velocity and direction of flow. On the other hand, properly spaced and pumped wells provide a mechanism to control the migration of leachate plumes (Section 14.3.5). Discharging and recharging well schemes are commonly used to restore contaminated aquifers.

Specific Capacity. The *static* water level in a well is the level prior to any pumping. The *drawdown* refers to the decline of the water level in a pumping well and is the difference between the static level and the level to which the water drops during pumping (Figure 2.17). The discharge rate of the well divided by the drawdown is the *specific capacity*. The specific capacity indicates how much water the well will produce per foot of drawdown and should not be confused with *specific yield* (Section 2.6.1). It can be calculated by the following equation:

$$\text{Specific capacity} = Q/s \quad (2.11)$$

where:

Q = discharge rate, in gpm

s = drawdown, in ft

If a well produces 100 gpm and the drawdown is 8 ft, the well will produce 12.5 gpm for each foot of available drawdown. Specific capacity is a useful measurement because it is easy to obtain, and multiplying specific capacity by 2000 gives a crude estimate of transmissivity (gpd/ft) for confined aquifers.

2.7 GUIDE TO MAJOR REFERENCES

Table 2.4 identifies major references in the following areas: (1) water resources and hydrology (which tend to focus on surface hydrology), (2) vadose zone hydrology, (3) hydrogeology, and (4) hydraulics. Most texts on hydrogeology will provide some coverage of surface and vadose zone hydrology and the hydraulics of ground-water flow, along with investigation methods, occurrence in different geologic settings, and ground-water chemistry. Heath (1983) serves as an excellent introductory text on hydrogeology. Freeze and Cherry (1979) is probably the most commonly cited intermediate hydrogeology text, but many other good texts are also available.

The hydraulics texts in Table 2.4 are divided into four major categories: (1) ground-water hydraulics, (2) porous media flow (which includes both saturated and unsaturated flow), (3) drainage and seepage, and (4) engineering hydraulics. Bear (1979) is probably the most widely cited text on ground-water hydraulics. Hydraulic principles are used in the design and analysis of aquifer pump tests. Major references focusing on pump test analysis are indexed in Table 7.5, and Table 7.6 provides an index to the primary literature on analytical solutions for aquifer tests.

Texts on drainage and seepage may be especially useful for design of hydrodynamic controls for ground-water protection or remediation (Section 14.4). Earlier editions and the current third edition of Cedergren (1989) is probably the most commonly used text in this category by the ground-water community. Individuals with a focus on engineering or agricultural applications may prefer other texts. Texts on engineering hydraulics tend to focus on flow in pipes and open channels.

Table 2.5 identifies major references on the characteristics of ground-water occurrence in the U.S. in the following categories: (1) national overviews, (2) regional summary appraisals prepared by the U.S. Geological Survey in the 1970s, (3) other regional assessments, and (4) state-specific reports. The Water Resources Division of USGS publishes foldouts for each state listing water resource publications and maps by USGS and cooperating agencies. These can be obtained from the USGS Water Resources Division District Office in a state, or the principal state water resource agency.

Figure 2.18 provides a geographic index to the 21 summary appraisals of ground-water resources that were published as USGS Professional Paper 813. The boundaries on this map are those established by the U.S. Water Resources Council for water resources regions in the U.S. and generally do not follow major hydrogeologic boundaries. These papers have also been reprinted as a single volume (Todd, 1983). Figure 2.19 shows the boundaries of major regional aquifers for which studies are under way or completed under the U.S. Geological Survey's Regional Aquifer System Analysis (RASA) program. Sun and Weeks (1991) provide a comprehensive bibliography of more than 800 USGS publications prepared under this program. Table 2.5 also includes a number of publications by the American Water Resources Association, prepared in cooperation with the U.S. Geological Survey's RASA program.

The U.S. Geological Survey has taken information from the RASA program and other available data to create a *Ground Water Atlas of the United States*. Regional areas of the atlas were published separately beginning in 1991, and upon completion, the separate chapters will be combined and available as a single volume. The chapters published as of 2002 are as follows:

Number of Regional Area	Chapter Content	Atlas Chapter	Year Published
—	Introductory material and nationwide summaries	730-A	
1	California, Nevada	730-B	1995
2	Arizona, Colorado, New Mexico, Utah	730-C	1995
3	Kansas, Missouri, Nebraska	730-D	1997
4	Oklahoma, Texas	730-E	1996
5	Arkansas, Louisiana, Mississippi	730-F	1998
6	Alabama, Florida, Georgia, South Carolina	730-G	1991
7	Idaho, Oregon, Washington	730-H	1994
8	Montana, North Dakota, South Dakota, Wyoming	730-I	1996

9	Iowa, Michigan, Minnesota, Wisconsin	730-J	1993
10	Illinois, Indiana, Kentucky, Ohio, Tennessee	730-K	1995
11	Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia	730-L	
12	Connecticut, Maine, Massachusetts, New Hampshire, New York, Rhode Island, Vermont	730-M	1995
13	Alaska, Hawaii, Puerto Rico, Virgin Islands	730-N	

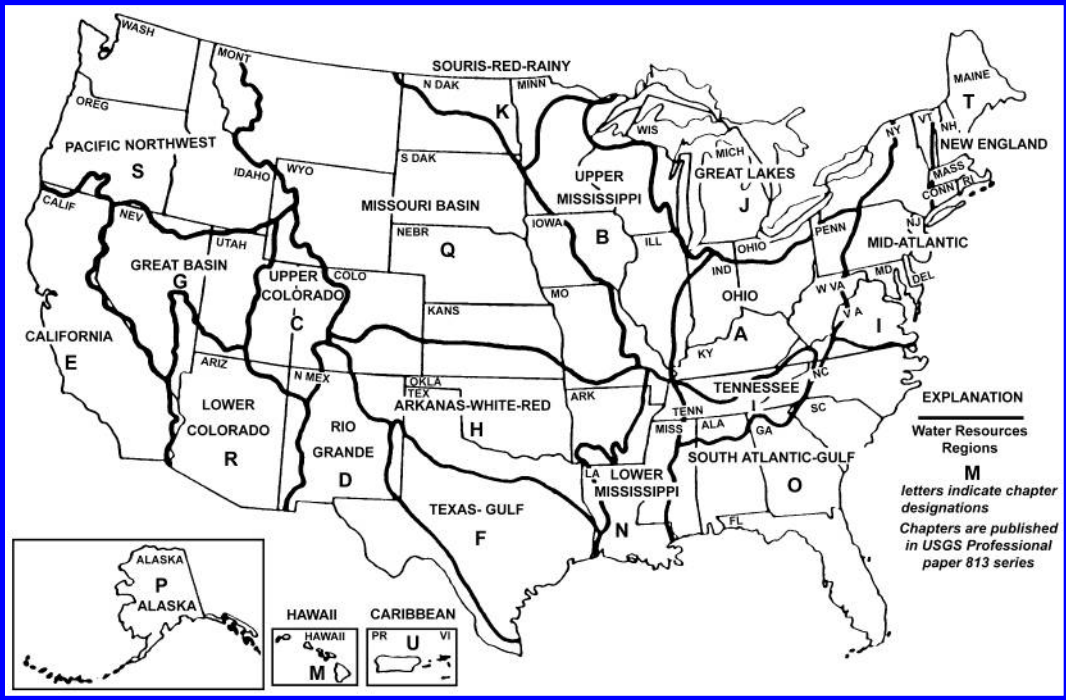


Figure 2.18 Geographic index to U.S. Geological Survey Professional Paper 813 ground-water reports.

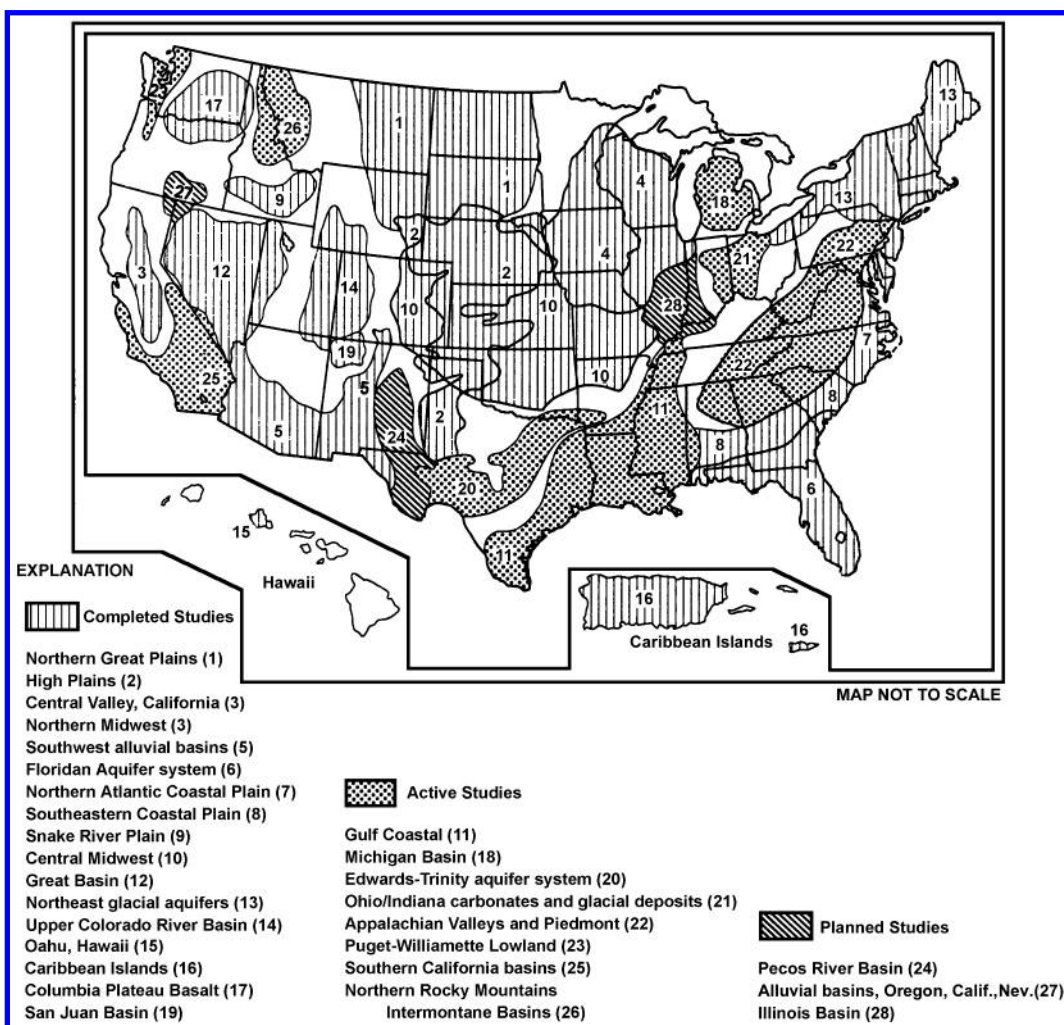


Figure 2.19 Geographic index to U.S. Geological Survey regional aquifer system studies (Sun and Weeks, 1991).

Table 2.4 Index to Major References on Surface and Vadose Zone Hydrology, Hydrogeology, and Hydraulics

Topic	References
Water Resources/ Hydrology	Black (1996), Bras (1990), Bowen (1982), Branson et al. (1981), Chow (1964), Chow et al. (1988), Downing and Wilkinson (1992), Dunne and Leopold (1978), Gray (1973), Grigg (1985), Kazmann (1988), Leopold and Langbein (1960), Linsley et al. (1949), Maidment (1993), Meinzer (1942), Newsom (1994), Rao and Hamed (1999 — flood frequency analysis), Rhoda (1985), Shaw (1988), Tebutt (1973), Todd (1970), van der Leeden et al. (1990), Viessman et al. (1977), Ward and Elliot (1995), Watson and Burnett (1993), Willis and Yeh (1987), Wisler and Brater (1959); <u>Engineering</u> : ASCE (1952), Butler (1957), Linsley and Franzini (1972), Linsley et al. (1958), Patra (2000), Skeat (1969), Shaw (1989), Wilson (1974)
Vadose Zone Hydrology	Guymon (1994), Looney and Falta (2000), Parlange and Hopkins (1999), Selker et al. (1999), Stephens (1995), Tindall and Kunkel (1999); <u>Soil Physics</u> : Baver et al. (1972), Campbell (1985), Childs (1969), Ghildyal (1987), Hanks (1992), Hanks and Ashcroft (1980), Hillel (1980a, 1980b, 1982, 1998), Jury et al. (1991), Kirkham and Powers (1972), Kohnke (1968), Koorevaar et al. (1983), Marshall and Holmes (1988), Warrick (2001); <u>Soil–Water Relations</u> : Hillel (1971), Iwata et al. (1994), Marshall (1960), Miyazaki (1993), Nielsen et al. (1972), Rode (1965); <u>Plant–Water Relations</u> : Slayter (1967); <u>Edited Volumes</u> : Hillel and Elrick (1990), Kienitz et al. (1991), Rijtema and Wassink (1969)
Hydrogeology ^a	<u>Bibliography/Glossary</u> : Dzhamalov et al. (1992), Lohman et al. (1972), Pfannkuch (1969), Poehls and Smith (2002), Porges and Hammer (2001), van der Leeden et al. (1991); <u>Introductory</u> : AWWA (1989), Baldwin and McGuiness (1963), Barton et al. (1985), Deming (2001), Heath (1980, 1983), Heath and Trainer (1981), Mills et al. (1985), Pinnaker (1983), Smith (1982), Rau (1970), Redwine et al. (1991), U.S. EPA (1985, 1990); <u>Intermediate-Advanced</u> : Bouwer (1978), Bowen (1980), Cooley et al. (1972), Custodio and Llama (1975), Davis and DeWiest (1966), Driscoll (1986), Fetter (2001), Fitts (2002), Freeze and Cherry (1979), Gelher (1993), Hudak (1999), Johnson (1966), Kovács et al. (1981), Manning (1997), Matthess (1982), McWhorter and Sunada (1981), Raghunath (1982), Todd (1980), Tolman (1937); <u>Field Hydrogeology</u> : Brassington (1998), Brown et al. (1983), Erdélyi and Gálfi (1988), Fletcher (1996), Hamill and Bell (1986), Mandel and Shiffton (1981), Moore (2002), Moss (1990), Sanders (1998), Sen and Sen (1995), Stone (1998), U.S. Geological Survey (1980), Walton (1970), Wright and Sondregger (2001); <u>Ground-Water Engineering</u> : De Marsily (1986), Delleur (1998), Hunt (1983), Kashaf (1986), Rethati (1984), Walton (1991); <u>Other Aspects</u> : Ingebritson and Sandford (1998 — in geologic processes), Lee (1998 — applied mathematics), Pyne (1995 — recharge and wells); <u>Edited Volumes</u> : Back and Freeze (1982), Back and Stephenson (1979), Back et al. (1988), Dillon and Simmers (1998), Gilbert et al. (1997), IAH (1985), IAHS (1967), Jones and Laenen (1992), Krothe and Jin (1997), Moore et al. (1989, 1991), Sakura (1993), Saleem (1976), Simpson and Sharp (1990), Soliman et al. (1997), Stober and Bucher (1999), Zaporozec (1990)
Chemical/Contaminant Hydrogeology Hydraulics ^b	See Table 4.5 <u>Fluid Mechanics</u> : Dodge and Thompson (1937), Streeter and Wylie (1979), Wang (2000), White (1974); <u>Ground-Water Flow</u> : Bear (1979), Bennett (1976), Bureau of Reclamation (1960, 1981), Campbell and Lehr (1973), Chapman (1981), Daly (1984 — flow lines), De Marsily (1986), DeWiest (1965), Edelman (1983), Freeze and Witherspoon (1967), Glover (1964, 1974), Halek and Svec (1979), Hantush (1964), Hubbert (1940, 1969), Hunt (1983), Jacob (1950), Lohman (1972), McWhorter and Sunada (1981), Peterson et al. (1952), Randkivi and Callender (1976), Rosenshein and Bennett (1984), Strack (1989), Verruijt (1982), Zijl and Nawalany (1993); <u>Porous Media Flow</u> : Bear (1972), Bear and Corapcioglu (1987), Bird et al. (1960), Brooks and Corey (1964), Case (1993 — unsaturated), Collins (1961), Corapcioglu (1991), Corey (1977 — heterogenous fluids), Cushman and Hall (1991), Dagan (1989), DeWiest (1966), Dullien (1979), Elrick (1972), Greenkorn (1983), IAHR (1972), Milne-Thompson (1968), Muskat (1937), Scheidegger (1960); <u>Drainage/Seepage</u> : Bear et al. (1968), Bureau of Reclamation (1968), Cedergren (1989), Craig and Gray (1985), Harr (1977), Luthin (1978), Marino and Luthin (1982), Powers (1992), Rushton and Redshaw (1979); <u>Engineering Hydraulics</u> : Colt Industries (1974), Hauser (1995), Lencastre (1987), Rouse (1950), Simon (1981)

^a See Table 1.4 for index of major references on karst geology, geomorphology, and hydrology. See Table 7.6 for major references on fractured rock hydrology.

^b References listed under hydrogeology will also cover hydraulics.

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* See Preface for information on how to obtain documents from CERL (U.S. EPA Center for Environmental Research Information) and NTIS.

Table 2.5 Index to Major References on Regional Hydrology and Ground Water in the U.S.

Topic	References
National	<u>Information Sources/Bibliographies</u> : Giefer (1976), Ralston (1975), Randolph and Deike (1966), Riggs (1962), Sun and Weeks (1991), USGS (1982, 1984, 1988a), U.S. Water Resources Council (1978a), van der Leeden et al. (1990); <u>Hydrologic Atlases</u> : Geraghty et al. (1973), Gerlach (1970), Langbein et al. (1949); <u>Ground Water Occurrence/Supply</u> : Aller et al. (1987), Back et al. (1988), Heath (1982, 1984), McGuinness (1963), Meinzer (1923), Thomas (1952); <u>Ground Water Quality</u> : See Table 4.4
Computer Databases	See Table 5.13
USGS Regional Summary Appraisals ^a	<u>East</u> : Boyd (1974 — Ohio region), Cederstrom et al. (1979 — South Atlantic Gulf), Sinnott (1982 — New England), Sinnott and Cushing (1978 — Mid-Atlantic), Weist (1978 — Great Lakes), Zurawski (1978 — Tennessee); <u>Central</u> : Baker and Wall (1976 — Texas-Gulf), Bedinger and Sniegocki (1976 — Arkansas-White-Red), Boyd (1975 — Upper Mississippi), Reeder (1978 — Souris-Red-Rainy), Taylor (1978 — Missouri Basin), Terry and Bryant (1979 — Lower Mississippi), West and Broadhurst (1975 — Rio Grande); <u>West</u> : Davidson (1979 — Lower Colorado), Eakin et al. (1976 — Great Basin), Foxworthy (1979 — Pacific Northwest), Price and Arnow (1974 — Upper Colorado), Thomas and Phoenix (1976 — California); <u>Noncontinental U.S.</u> : Gomez-Gomez and Heisel (1980 — Caribbean), Takasaki (1978 — Hawaii), Zenone and Anderson (1978 — Alaska)
Other Regional	<u>Atlantic/Gulf Coastal Plain</u> : Johnston and Bush (1988), USGS (1987, 1988b), Vecchioli and Johnson (1987) ^b ; <u>Basin and Range</u> : Bedinger et al. (1989); <u>Caribbean</u> : Gomez-Gomez et al. (1991) ^b ; <u>Midwest</u> : Swain and Johnson (1989) ^b ; <u>Northeast Glacial Aquifers</u> : Randall and Johnson (1992) ^b ; <u>Southeast</u> : Hotchkiss and Johnson (1992) ^b ; <u>Southwest Alluvial Basins</u> : Anderson and Johnson (1986) ^b ; <u>Western Mountain Area</u> : McLean and Johnson (1988) ^b ; <u>Far West</u> : Prince and Johnson (1992) ^b , Smith (1988)
States	Giefer and Todd (1972, 1976); <u>Alabama</u> : Avrett (1968); <u>Alaska</u> : Fuelner et al. (1971), U.S. Water Resource Council (1978c); <u>Colorado</u> : Robson (1987); <u>Hawaii</u> : Mink (1977), Stearns (1946), U.S. Water Resource Council (1978b); <u>Florida</u> : Franks (1981), Hyde (1975), Southeastern Geological Society (1986); <u>Idaho</u> : Graham et al. (1981), Yee and Souza (1987); <u>Indiana</u> : Marie (1976); <u>Massachusetts</u> : Massachusetts Department of Environmental Quality Engineering (1986); <u>Mississippi</u> : Mitchell (1986); <u>South Dakota</u> : Meyer (1986); <u>Washington</u> : Molennar et al. (1980)

^a Reports with state names do not strictly follow state boundaries — see Figure 2.18; also published as a single volume (Todd, 1983).

^b Published in AWR/USGS Regional Aquifer System Analysis (RASA) program series; see Sun and Weeks (1991) for a bibliography of USGS RASA publications and Figure 2.19 for region boundaries.

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CHAPTER 3

Soil and Ground Water Geochemistry and Microbiology

Understanding the basic geology and subsurface flow patterns is only the first step in studying contaminated soils and ground water. The rate and distance of transport of any specific contaminant will be strongly influenced by physical, geochemical, and microbiological processes. Such processes may reduce or enhance the mobility of a contaminant. These processes may transform a contaminant to substances that may be less or more toxic than the original contaminant.

The physical and chemical interactions of individual contaminants with existing environmental conditions of the soil will affect the amount of contaminant that reaches the ground water and the concentrations in contaminant plumes. These geochemical and microbiological processes will also largely determine what combination of remediation techniques will be required if cleanup becomes necessary.

The same difficulties inherent in studying ground-water flow (limited direct observation and variability of geologic materials) apply equally to subsurface chemistry and microbiology. In fact, the difficulties are compounded because of the large number of geochemical reactions that are possible and the fact that the outcome of these reactions will vary depending on environmental conditions such as pH, Eh (redox potential), salinity, mineralogy of the solid matrix, temperature, and pressure. Nevertheless, steady advances in the study of the geochemistry and microbiology of soil and ground-water systems in recent years provide a basis for developing a qualitative analysis of the potential behavior of many contaminants in the subsurface.

This chapter begins by discussing key characteristics of chemical systems (Section 3.1), followed by identification of major subsurface chemical distribution processes (Section 3.2), transformation processes (Section 3.3), and environmental parameters that affect chemical processes (Section 3.4). The chapter concludes by describing basic concepts related to microbial ecology of the subsurface (Section 3.5).

3.1 KEY CHARACTERISTICS OF CHEMICAL SYSTEMS

A chemical system is a mixture of individual chemical components. *Homogeneous* systems consist of components in one phase of matter (solid, liquid, or gas), whereas *heterogeneous* systems contain two or more phases. A chemical system can be described by the interactions that occur within it and by the effects that these processes have on the system's chemical composition and phases. Interactions that change the chemical structure of system components are called chemical

reactions. Other interactions, such as processes that alter the solubility of system components, change the system without altering chemical structures.

3.1.1 Equilibrium, Thermodynamics, and Kinetics

The *equilibrium* state implies that as long as no significant changes in major components or environmental factors affect the system, the chemical speciation and phases of the system will tend toward a specific composition. An equilibrium state does not imply that chemical processes cease. Within the time frames of observation, the rates of equilibrium reactions in the forward direction (i.e., toward products) can be related to the rate of the reverse reactions by the equilibrium constant.

In nonequilibrium systems, chemical processes act to alter the chemical composition or phase of the system, and equilibrium predictions may not apply. Simple systems, such as mixtures of sodium chloride and water, attain solution equilibrium relatively rapidly. More complex systems, particularly those involving solution and solid phases, may never reach equilibrium under normal environmental conditions.

Thermodynamically, a chemical system is in equilibrium when its free energy is minimized. Thus *thermodynamic* principles define the stability of substances within the system and whether a reaction can occur. If complex solid–liquid systems are perturbed by the introduction of a contaminant species or phase, chemical reactions will proceed and it may be very difficult to predict the approach to equilibrium. *Exothermic* chemical reactions release energy in the form of heat, and *endothermic* reactions require an input of energy to take place. At equilibrium, reactions may continue, but for every exothermic reaction there will be a compensating endothermic reaction such that the overall distribution of chemical species remains the same. Geochemical distribution-of-species computer codes are based primarily on equilibrium thermodynamic principles (Section 10.3.3).

Thermodynamic calculations can predict whether a chemical reaction is likely to occur under specified conditions, but they give no indication of how fast the reaction will occur. *Kinetics* describes the rate of chemical reactions. Some reactions, such as the ionization of a strong acid in water (Section 3.2.1), will occur almost instantaneously. These reactions often occur in one or more concerted steps. Other reactions, such as the hydrolysis of cyanides at low pH (Section 3.3.2), may take tens of thousands of years. Complex, multistep reactions involving several chemical species and their solution equilibria may have very complicated rate laws. Three empirically derived rate laws can be used to approximate the rates of concerted chemical processes (Bedient et al., 1982):¹

$$dC_A/dt = -k_0 \quad \text{Zero order}$$

$$dC_B/dt = -k_1 C_A \quad \text{First order}$$

$$dC_B/dt = -k_2 C_A C_B \quad \text{Second order}$$

where:

k_0 , k_1 , k_2 = rate constants (mol/l-sec, /sec, l/mol-sec, respectively)

C_A , C_B = some reacting species

The rate of zero-order reactions proceeds independently of concentration, whereas the speed of first-order reactions is directly proportional to the concentration of a single reacting species. Higher-order reaction kinetic rates depend on the relative concentration of several reacting species. Fractional kinetic orders are quite common in reactions that occur in solution where several

¹ Bedient, P.B., N.K. Springer, C.J. Cook, and M.B. Tomson. 1982. Modeling Chemical Reactions and Transport in Groundwater Systems: A Review. In: Modeling the Fate of Chemicals in the Aquatic Environment, K.L. Dickson, A.W. Maki, and J. Cairns, Jr. (eds.), Ann Arbor Science, Ann Arbor, MI, pp. 215–246.

Table 3.1 Characteristics of Chemical Processes That May Be Significant in the Subsurface

Characteristic	Types of Reactions
Homogeneous	Acid–base, hydrolysis, hydration, neutralization, oxidation–reduction, polymerization, thermal degradation
Heterogeneous	Adsorption–desorption, precipitation–dissolution, immiscible phase separation, biodegradation, complexation
Reversible	Acid–base, neutralization, oxidation–reduction (biologically mediated), adsorption–desorption, precipitation–dissolution, complexation
Irreversible	Hydrolysis, oxidation–reduction (inorganic), biomineralization, immiscible phase separation

Source: Boulding (1990).

equilibria control the concentrations of speciation of reactive chemical species. Most solute transport computer codes assume first-order kinetics when modeling ground-water systems (Section 10.3.2).

3.1.2 Heterogeneity and Reversibility

Chemical processes can be broadly classified as either homogeneous or heterogeneous and as either reversible or irreversible (Table 3.1). *Homogeneous* reactions in ground water take place in only the aqueous phase. In general, these reactions occur uniformly throughout the phase and are typically easier to study and predict than heterogeneous reactions. *Heterogeneous* reactions tend to occur at the interface between different phases, thus involving more than one phase. An example is sorption. Some reactions, such as precipitation, may result in phase changes. Heterogeneous reactions also tend to occur more actively at some locations in the chemical system than at others. Bacterial decomposition of wastes is an example of a complex heterogeneous process that may be more active in locations with conditions favorable for organisms and less active in other, less favorable locations.

The *reversibility* of specific chemical reactions is another important characteristic in assessing the fate of contaminants in ground water. Depending on environmental conditions, reversible reactions may proceed in either one or both directions. Acid–base reactions exemplify reversible processes. In aqueous solutions, relatively minor changes in factors such as pH or concentration or reactants can change the direction of these reactions. Irreversible reactions, typified by hydrolysis, have a strong tendency to go in one direction only.

Table 3.1 lists several reversible and irreversible processes that may be significant in ground water. The characteristics of the specific contaminant and the environmental factors present in an aquifer (Section 3.4) strongly influence which processes will occur and whether they will tend to be irreversible. Irreversible reactions are of particular interest in the study of contaminants in ground water. A contaminant that is rendered nontoxic through irreversible reactions may be considered to be permanently transformed to a nonhazardous state.

3.1.3 Phases and Speciation

Chemical reactions may result from interactions among solids, liquids, and gases. The major interactions that occur between contaminants and the subsurface include:

- *Liquid–liquid interactions.* These occur when nonaqueous phase liquids (NAPLs) reach the water table.
- *Liquid–solid interactions.* Water itself can react chemically with solids in the subsurface. Also contaminants dissolved in water may react with solids through sorption or ion exchange.
- *Liquid–gas interactions.* Volatile NAPLs such as benzene and carbon tetrachloride may shift to a vapor phase in the vadose zone. This may also occur with dissolved volatile organic contaminants at the interface between the water table and the vadose zone.

A substance may exist in several forms, or *species*. Five major types occur in ground water:

1. “Free” ions are surrounded only by water molecules and are very mobile in ground water. Acid–base (Section 3.2.1) and dissolution reactions (Section 3.2.3) create free ions.
2. Insoluble species may exist in solid form (such as Ag_2S and BaSO_4) or liquid form (such as gasoline). Precipitation reactions (Section 3.2.3) and immiscible phase separation (Section 3.2.4) are important processes affecting this type of speciation.
3. Metal–ligand complexes (such as $\text{Al}(\text{OH})^{2+}$ and Cu–humate) and organic–ligand complexes tend to be mobile in ground water (see Section 3.3.1).
4. Physically or chemically sorbed species are immobile in ground water but can be remobilized if replaced by other species with a stronger affinity to the solid surface or via transformation reactions (see Section 3.2.2).
5. Species may differ by oxidation state (manganese (II) and (IV), iron (II) and (III), and chromium (III) and (VI)). Oxidation state is influenced by the redox potential (see Section 3.3.3). Mobility is affected because oxidation state influences precipitation–dissolution reactions (Section 3.2.3) and also toxicity in the case of heavy metals.

Dissolved species may be either ionic or nonionic. *Ionic* species possess a net positive or negative charge. *Nonionic* species are neutral molecules that have no net excess charge. *Cations* are positively charged ions (Na^+ , Ca^{2+}), and *anions* are negatively charged (SO_4^{-2}). The ability of solids with a net neutral charge to dissociate into ionic species is more common with inorganic contaminants than with organic contaminants. Acid–base reactions (Section 3.2.1) and hydrolysis reactions (Section 3.3.2) often determine the distribution between ionic and nonionic species.

Neutral substances may be either nonpolar or polar. In *nonpolar* species there is no overall excess charge. In *polar* species, the chemical structure stabilizes charged poles on the molecule, even though the net charge is zero. Water (H_2O) is a polar molecule with the positive pole on the side of the hydrogen atom and the negative pole on the side of the oxygen atoms. Nonpolar molecules tend to be *hydrophobic* (water avoiding) for reasons discussed in Section 3.2.2.

Many substances may exist as several species in the subsurface depending on geochemical conditions. Identifying active chemical forms of an element and predicting the reactivity in the vadose and the saturated zones is an essential part of evaluating the fate and transport of contaminants.

3.1.4 Distribution vs. Transformation Processes

Geochemical processes in the subsurface can be broadly classified into distribution processes and transformation processes. *Distribution processes* affect the form or state of association of a specific chemical substance in the aqueous or solid at a given time or under specific environmental conditions. Thus, a substance may be associated with a solid phase or in solution (described by the distribution processes). Regardless of the phase, the chemical properties and toxicity of chemical species may remain unaltered. The physical state of a substance, however, influences the transformation and transport processes that can occur. For this reason, distribution processes are important to define during a fate assessment.

Transformation processes alter the chemical structure of a substance. In the subsurface, the transformation processes that may occur are largely determined by the conditions created by distribution processes, reactivity, and the prevalent environmental factors. Transport processes may not need to be considered if transformation processes irreversibly change a hazardous waste to a nontoxic form.

Table 3.2 lists major distribution and transformation processes and also indicates whether processes are biotic (mediated or initiated by organisms in the environment), abiotic (not involving biological mediation), or both. Biotic processes are often limited to environmental conditions that favor growth of the organisms that are capable of transforming a particular compound. Abiotic processes, on the other hand, can generally occur under a wide range of environmental conditions.

Table 3.2 Significance of Chemical Processes in the Subsurface

Process	Detoxication	Mobility	Biotic/Abiotic
Phase Distribution			
Acid–base equilibrium	No	Yes	Both
Adsorption–desorption	No	Yes	Abiotic
Precipitation–dissolution	No	Yes	Abiotic
Immiscible phase separation	No	Yes	Both
Volatilization	No	Yes	Abiotic
Transformation			
Biodegradation	Yes	Yes	Biotic
Complexation	No	Yes	Abiotic
Hydrolysis	Yes	Yes	Both
Neutralization	Yes	No	Abiotic
Oxidation–reduction	Yes	Yes	Both

Source: Boulding (1990).

Volatilization, neutralization, sorption, precipitation, and complexation are abiotic processes, though they may be catalyzed by biochemical factors.

3.2 SUBSURFACE DISTRIBUTION PROCESSES

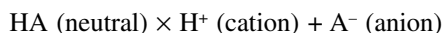
Phase distribution usually does not affect the toxic properties of the substance. It can, however, affect the mobility of the contaminants in the subsurface. The major distribution processes and the sections in which they are discussed are as follows:

- Acid–base equilibrium ([Section 3.2.1](#))
- Sorption ([Section 3.2.2](#))
- Precipitation–dissolution ([Section 3.2.3](#))
- Immiscible phase separation ([Section 3.2.4](#))
- Volatilization ([Section 3.2.5](#))

3.2.1 Acid–Base Equilibria

Acid–base equilibrium reactions affect pH, a function of the concentration of hydrogen ions in solution, which is a controlling factor in the type and rate of many other chemical reactions (see [Section 3.4.1](#)).

Acids ionize in solution to form hydrogen ions and anions according to the general reaction:



As the equation shows, the ionization is reversible. The acid anion (acting as a weak base) can recombine with the hydrogen ion to reform neutral HA. Both reactions occur continuously in solution, with the extent of ionization dependent on the strength of the acid. Strong acids, such as HCl, ionize completely in dilute aqueous solution. Thus, a 0.01 molar (10^{-2} molar) solution has a pH of 2. Weak acids, such as acetic acid and other organic acids, do not ionize completely in aqueous solution and form solutions with pH generally ranging from 4 to 6.

In the above example, the acid anion A^- functions as a base when it combines with a hydrogen ion. By definition, any substance that combines with hydrogen ions is a base. Like strong acids, strong bases ionize completely in dilute aqueous solution. Thus, NaOH dissolves in water to form

hydroxide ions, which in turn function as a base when they combine with hydrogen ions to form water, as shown by the general equation:



Acid–base equilibrium reactions generally occur quickly. When the pH of a solution changes, acids and bases readily attain a new equilibrium between neutral and ionic forms. Weak acids or weak bases have little influence, if any, on the pH of the aqueous solution. Mills et al. (1985/T2.4) describe the procedures for calculating the fraction of a toxic organic acid or base that is in the nonionic, neutral form. This procedure is especially useful for evaluating the volatilization of organics at near-surface conditions (because only electrically neutral species are directly volatile).

3.2.2 Sorption

Sorption is a phase-distribution process in which dissolved metals or toxic organics (solutes) are transferred from the aqueous phase (water) to the solid phase (rock, soil, or particles of organic matter). Sorption is a major mechanism affecting the mobility of heavy metals and toxic organic substances and is thus a major consideration when assessing transport. *Adsorption*, which occurs on the solid–solution interface, such as on clays, is usually fully or partly reversible (desorption). Although adsorption does not directly affect the toxicity of a substance, the substance may be rendered nontoxic by transformation processes, such as hydrolysis, while it is adsorbed. *Absorption* is a process whereby a chemical specie may be sorbed into the solid matrix material, such as with activated charcoal. In some respects it may be considered solid–solution formation. Absorption may occur after surface sorption or adsorption has occurred.

Sorption is a widespread chemical phenomenon that has been studied by many different disciplines, resulting in a diverse and often confusing terminology. Thus, the general term *sorption* is often used where the distinction between adsorption and absorption is not clear. In this handbook, the term *sorption* is used to describe any one of a number of intermolecular interactions involved in phase distribution from the aqueous to the solid phase. Under carefully controlled laboratory conditions, individual sorption mechanisms can be studied, but in the real world, sorption is the result of multiple processes acting on both multiple species and solid surfaces. In fact, the distinction between sorption and precipitation is not easily made at the liquid–solid interface (Sposito, 1984/T3.12).

Sorption and desorption are caused by interactions between molecules in solution and those in the structure of solid surfaces. Many chemical and physical properties of both aqueous and solid phases affect sorption, and the physical chemistry of the process itself is complex. For example, sorption of one ion or neutral specie may result in the desorption of another (see discussion of ion exchange below).

Sorption reactions are often exothermic (Section 3.1.1), and sorption processes can be broadly classified into two groups based on the energies involved: chemical sorption (high energy) and physical sorption (low energy). Sorption can also be described in terms of type of bond and forces involved. Table 3.3 summarizes these parameters and also lists the type of contaminant that is most likely to be involved in the different types of bonds.

Chemical sorption (also called chemisorption) involves the formation of chemical bonds between the sorbate molecule and the sorbent surface. Ion exchange, protonation, and hydrogen bonding are examples of chemical sorption processes (see Table 3.3). These bonds typically involve energies on the order of 10 kcal/mol. In *ion exchange*, a cation at a negatively charged site on a mineral surface is replaced by another cation. The cation exchange capacity measures the sorption capacity of a material (see discussion of clay minerals in Section 1.1.1). Anions such as sulfate and nitrate may also be sorbed, but at much lower levels than cations because many mineral surfaces are negatively charged. *Protonation* involves the attachment of a molecule to a previously sorbed

Table 3.3 Major Intermolecular Interactions Involved in Sorption in the Subsurface

Type of Bond/Attraction	Forces	Sorbate	Energy (kcal/mol)
Chemical Bonds			
Ion exchange	Electrostatic	Metal cations Organic acid/cation	Up to 50
Protonation	Electrostatic	Organic bases	Up to 35
Hydrogen	Electrostatic	Polar organic	0.5–15
Physical Sorption Forces			
Van der Waals	Electrostatic	Small molecules Large molecules	1–2 11+
Hydrophobic	Entropically driven	Nonpolar organic	1

Source: Boulding (1990).

hydrogen ion by an acid–base reaction. *Hydrogen bonds* result from the attraction of polar molecules to hydrogen atoms in already sorbed molecules or ionic species.

Physical sorption processes involve physical forces and are associated with lower energies, typically less than 10 kcal/mol. *Van der Waals* attractions are weak electrostatic forces that operate between all atoms, ions, and molecules. *Hydrophobic bonds* involve the “pushing” of nonpolar organic molecules toward solid surfaces by polar water molecules to achieve a more thermodynamically stable liquid structure (Table 3.3).

3.2.3 Precipitation and Dissolution

Precipitation is a phase-distribution process whereby insoluble solids are formed and separate from a solution. Dissolution involves a change from the solid or gaseous phase to the aqueous phase. The solubility of a compound, its tendency to dissolve in water or other solutions, is the main property affecting the precipitation–dissolution process. In the subsurface, precipitation–dissolution reactions are often evaluated by the use of mineral stability diagrams that delineate the pH, Eh (or pe), temperature, and pressure conditions under which a particular mineral is stable. [Figure 3.1](#) illustrates such a diagram for the iron in water.

Precipitation reduces mobility, and dissolution increases mobility of contaminants. Ionic precipitation–dissolution reactions are often fully reversible. Precipitation can only be considered to effectively immobilize a contaminant if environmental conditions in an aquifer are sufficiently stable to prevent dissolution from occurring at some future time.

The equilibrium concentration of a compound in water is determined by its *equilibrium solubility*, or *solubility product constant*, the maximum amount of a compound that will dissolve in a solution at a specified temperature and pressure. The solubility of toxic organic compounds is generally much lower than that of inorganic salts, a characteristic that is particularly true of nonpolar compounds because of their hydrophobic character. Equilibrium solubility will change with changing environmental parameters such as temperature, pressure, and pH. For example, the solubility of many organic compounds increases when solution temperature is increased.

Precipitation may occur when the concentration of a compound in solution exceeds the equilibrium solubility. For organic chemical wastes, precipitation is not generally a significant phase-distribution process in the subsurface, although in certain circumstances, it may need to be considered. For example, pentachlorophenol tends to precipitate from aqueous solution when the solution has a pH of less than 5 (Choi and Aomine, 1974).² Polychlorophenols form insoluble precipitates

²Choi, J. and S. Aomine. 1974. Mechanisms of Pentachlorophenol Adsorption by Soils. *Soil Sci. Plant Nutr.* 20(4):371–379.

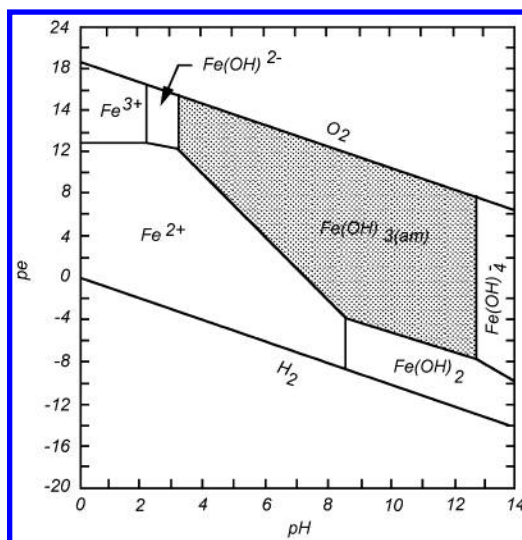


Figure 3.1 pe-pH diagram for the Fe-H₂O system (Palmer and Fish, 1991).

in water that is high in Mg²⁺ and Ca²⁺ ions (Davis, 1967/T3.12). Also, organic anions react with such elements as Ca²⁺, Fe²⁺, and Al³⁺ to form sparingly soluble to nearly insoluble compounds.

Precipitation reactions are most likely to be significant for heavy metals and other inorganic species in ground water. For example, sulfide ions precipitate with metal ions as metal sulfides. Biological activity caused by organic contaminants may initiate redox reactions resulting in the precipitation of iron and manganese oxides (see [Section 3.3.3](#)). Mixing of ground waters from different aquifers or injection by artificial recharge may cause precipitation and dissolution reactions. Precipitation reactions can lead to plugging of injection or monitoring wells.

Coprecipitation is a phase-distribution process whereby metal ions precipitate from the aqueous phase even if the equilibrium solubility has not been exceeded. This process occurs when metals are incorporated into the crystal lattice structure of silicon (Si), aluminum (Al), and iron (Fe) oxides when these latter compounds precipitate out of solution. The incorporation of metals in coprecipitated solids varies. Iron oxides and hydroxides may incorporate a number of metal ions, such as chromium (Cr), nickel (Ni), arsenic (As), selenium (Se), cadmium (Cd), and thorium (Th), during precipitation. Coprecipitation with carbonate minerals may be an important mechanism for removal of Co, Pb, Zn, and Cd (Förstner and Wittmann, 1981/T4.5).

Cosolution is a process by which mixing of several water-miscible organic solvents (such as ethanol, methanol, and acetone) with ground water increases the solubility of hydrophobic organic contaminants. Cosolvents reduce hydrophobicity by increasing the interactions between the solute and the solvent, thereby decreasing physical sorption (Nkedi-Kizza et al., 1985).³ For hydrophobic contaminants, the presence of biologically derived or anthropogenic compounds in the range of 20% or greater by volume increases their solubility by an order of magnitude or more.

3.2.4 Immiscible Phase Separation

A liquid or a gas that is poorly soluble in water may separate from the water, resulting in an immiscible phase. Nonaqueous phase liquids (NAPLs) that are lighter than water (LNAPLs) will tend to float on the surface of the water table, and those that are denser than water (DNAPLs) will

³ Nkedi-Kizza, P., P.S.C. Rao, and A.G. Hornsby. 1985. Influence of Organic Cosolvents on Sorption of Hydrophobic Organic Chemicals by Soils. *Environmental Science and Technology* 19:975-979.

tend to sink to the bottom of aquifers. The behavior of NAPL contaminants in the subsurface is described in more detail in Section 4.4.3 (Density/Viscosity Differences).

3.2.5 Volatilization

Transfer of contaminants from the free-product or aqueous phase to the gaseous phase is called *volatilization*. Volatilization is not a major process in the natural subsurface, but it is very significant when contaminants such as chlorinated solvents and petroleum-based liquids are involved. Major factors that affect volatilization include (1) the area of contact between the free products and the unsaturated zone, (2) the vapor pressure of the spilled compound, and (3) the rate at which the compound diffuses in the subsurface. Contaminants with vapor pressures above 14 mmHg at 20°C are generally volatile enough to use soil vapor extraction (Section 13.2.1) as a remediation technique.

3.3 SUBSURFACE TRANSFORMATION PROCESSES

Transformation processes change the chemical structure of a compound. The evaluation of contaminants in the subsurface must consider both the full range of transformation processes that may occur and the toxicity and mobility of the resulting reaction products. Transformation processes in the subsurface may result in one or more of the following:

- *Detoxification*, an irreversible change in a substance from a toxic to a nontoxic form. This occurs most commonly when an organic substance breaks down into its inorganic constituents, with water and carbon dioxide being the main by-products.
- *Transtoxification*, the conversion of one toxic compound to another toxic compound. In the process, toxicity may remain the same, increase, or be reduced. For example, tetrachloroethylene is readily degraded under anaerobic conditions to vinyl chloride, which is both more mobile and more toxic than the original compound.
- *Toxification*, the conversion of a nontoxic compound to a toxic substance.

The major transformation processes in the subsurface are complexation (Section 3.3.1), hydrolysis (Section 3.3.2), oxidation–reduction (Section 3.3.3), and biotransformation (Section 3.3.4). Two additional transformation processes, polymerization and thermal degradation, occur less frequently and are discussed briefly in Section 3.3.5 along with catalysis, which may facilitate the occurrence of various transformation processes.

3.3.1 Complexation

A complex ion is one that may contain several molecules or ionic species. Metal ions in solution commonly form complexes with water, chloride, and other species that are called *ligands*. Depending on the structure and reactivity of a contaminant, complexation by inorganic or organic ligands may increase or decrease its mobility, reactivity, and persistence. Because of these effects, complex formation is a very important process for transition series metals (i.e., Fe, Mn, Co, Ni, Zn, Cu) and may also be significant for some organic contaminants. Heavy metals (i.e., Pb, Cd, Hg) are particularly prone to complexation because their atomic structure (specifically the presence of unfilled d orbitals) favors the formation of bonds with polar molecules, such as water or ammonia (NH₃) and anions such as chloride (Cl[−]) and cyanide (CN[−]).

Complex formation is likely in solutions with high ionic strength, because the large number of ions present in solution increases the number of chemical species that can form. Many variables affect the stability of a complex ion relative to ions and metals that can serve as potential ligands to the central metal, the most important of which are the valence (charge) and radius of the central

cation. As a rule, the stability of complexes formed with a given ligand increases with cation charge and decreases with cation radius (Langmuir, 1979).⁴

The total solubility of metals is often much higher when they are in the form of organometallic complexes. Naturally occurring chemicals that can partially complex with metal compounds and increase the solubility of the metal include aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, and phenols.

Chelation is the process of forming complex ions with organic ligands that have more than one functional group available for bonding to the central metal ion in the complex. The complex ion formed by this process is called a *chelate*. The ligands in chelates are classified according to the number of binding sites in the molecule: monodentate (one site), bidentate (two sites), etc. Metal solubility (i.e., mobility) is often substantially increased when chelation occurs, and metal–chelate compounds are very stable when the metal ion is chelated by a heterocyclic ring of an organic molecule. Many simple organic–metal complexes will tend to dissociate if solutions become more dilute. Often chelated complexes do not (Martell, 1971).⁵ Even sorbed metals may be remobilized into solution by organic chelates. For example, the synthetic chelate nitrilotriacetic acid (NTA) has been used as a detergent–builder alternative to polyphosphate in detergents. NTA has been observed to remobilize sorbed heavy metals in the near-surface environment (Förstner and Wittmann, 1981/T4.5).

Metal ions in solution readily form complex ions by the process of *hydration* (bonding to water molecules). Because of the dipolar nature of water molecules, the oxygen atoms with a slight excess negative charge are attracted to the positively charged metal ion. Hydration tends to increase the complexity of chemical reactions because hydrated polyvalent metal ions may form multiple associations with other metals to create complex polynuclear ions. Hydration may also reduce mobility of metal ions through physical sorption. However, mobility can also be reduced by dehydration when organic ligands replace water molecules in complex ions. Polynuclear metal ions and large organic complexes can be readily sorbed onto mineral surfaces because of their large molecular weights, which enhance the sorption processes (Section 3.2.2).

3.3.2 Hydrolysis

Hydrolysis occurs when a compound reacts chemically with water, and new chemical species are formed by the reaction. Hydrolysis reactions fall into two major types:

- *Replacement* is the most common hydrolysis reaction. In this reaction, one functional group is replaced by an –OH (hydroxide ion) originating from a water molecule. For example, a hydroxide ion can replace the halide ion in an alkyl halide to form a soluble alcohol, leaving the halide ion in solution.
- *Addition reactions* involve the incorporation of water into the chemical structure of a compound. An example of this type of reaction is that by which alcohols can form by the addition of water to a carbon–carbon double bond.

Replacement and addition reactions are essentially irreversible transformation processes and may result in intermediate compounds that are subject to further hydrolysis (e.g., nitriles to amides and then onto acids). Whether hydrolysis results in detoxification, transtoxification, or toxification depends on the toxicity of the most stable end product of any series of hydrolysis reactions.

Hydrolysis is easily predicted, provided that the necessary rate constants for a compound are known. The rate of abiotic hydrolysis is given by the equation

⁴ Langmuir, D. 1979. Techniques of Estimating Thermodynamic Properties for Some Aqueous Complexes of Geochemical Interest. In: Chemical Modeling in Aqueous Systems: Speciation, Sorption, Solubility and Kinetics, E.A. Jenne (ed.), ACS Symposium Series 93, American Chemical Society, Washington, D.C., pp. 353–387.

⁵ Martell, A.E. 1971. Principles of Complex Formation. In: Organic Compounds in Aquatic Environments, S.D. Faust and J.V. Hunter (eds.), Marcel Dekker, New York, pp. 239–263.

$$R = -k_H C_T \quad (3.1)$$

where:

R = the rate of hydrolysis, $\text{mol l}^{-1}\text{sec}^{-1}$ or $\mu\text{g l}^{-1} \text{sec}^{-1}$

k_H = specific hydrolysis rate constant, sec^{-1}

C_T = the dissolved plus adsorbed phase concentration of compound C , mol l^{-1} or $\mu\text{g l}^{-1}$

The hydrolysis rate constant, k_H , is actually the sum of three rate constants:

$$k_H = k_n + k_a[H^+] + k_b[OH^-] \quad (3.2)$$

where:

k_n = the neutral hydrolysis rate constant for the pH-independent reactions of a chemical with water, sec^{-1}

k_a = the acid-catalyzed hydrolysis rate constant, $\text{l mol}^{-1} \text{sec}^{-1}$

$[H^+]$ = the concentration of hydrogen ion, mol l^{-1} ($[H^+] \times 10^{-\text{pH}}$)

k_b = the base catalyzed hydrolysis rate constant, $\text{l mol}^{-1} \text{sec}^{-1}$

$[OH^-]$ = the concentration of hydroxide ion, mol l^{-1} ($[OH^-] \times 10^{-14}$)

In an acid solution, $k_b = 0$, and in an alkaline solution, $k_a = 0$. Also, hydrolysis of most volatile organic compounds is not acid catalyzed ($k_a = 0$). When the substrate is dilute and the pH is well buffered, Equation 3.2 for VOCs simplifies to (Washington, 1995):⁶

$$k_H = k_n + k_b \quad (3.3)$$

Hydrolysis of some organic compounds, such as carbon tetrachloride, is independent of acid or base concentration ($K_a = 0$), so $K_H = k_n$. On the other hand, the chlorinated methanes chloroform, dichloroethane, and chloroethane have neutral and base-catalyzed rate constants, so Equation 3.3 applies (Jeffers et al., 1989).⁷

Laboratory hydrolysis measurements are typically done at very high temperatures to shorten the time required for the experiment. The Arrhenius equation is commonly used to adjust the K_H to the temperature of interest:

$$K_{\text{obs}} = A^{(-E/RT)} \quad (3.4)$$

or

$$\log k = \log A - (E/RT) \quad (3.5)$$

where:

K_{obs} = pseudo-first-order rate constant describing observed rate of substrate consumption

A = Arrhenius constant preexponential factor

E = activation energy

R = universal gas constant (0.01914 kJ/mol K)

T = absolute temperature in degrees Kelvin

⁶ Washington, J.W. 1995. Hydrolysis Rates of Dissolved Volatile Organic Compounds: Principles, Temperature Effects and Literature Review. Ground Water 33:415–424.

⁷ Jeffers, P.M., L.M. Ward, L. Woytowitz, and N.L. Wolfe. 1989. Homogeneous Hydrolysis Rate Constants for Selected Chlorinated Methanes, Ethanes, Ethenes and Propanes. Environmental Science and Technology 23(8):965–969.

At any fixed pH, the half-life of a substance is independent of concentration and can be calculated with the equation

$$t_{1/2} = \ln(2)/K_H = 0.693/k_H \quad (3.6)$$

Hydrolysis reaction rates are commonly reported in terms of half-life, the time it takes for half of the original concentration of the substance to be hydrolyzed. Hydrolysis half-lives of various hazardous organic contaminants range from days to thousands of years. Hydrolysis rates greatly depend on pH and also vary widely for an individual compound under acidic to basic conditions. Hydrogen cyanide illustrates the strong effect that pH can have on hydrolysis rates. Cyanides hydrolyze to amides, which then hydrolyze to acids and ammonia. At a pH of greater than 10, this reaction has a half-life of about 10 years. At a pH of 4, however, the reaction takes over 10,000 years (Scrivner et al., 1986).⁸ Furthermore, metal–cyanide complexes do not hydrolyze readily. These complexes can reduce the concentration of free cyanide in solution, but they can also increase the time needed for the total cyanide concentration to decrease due to hydrolysis.

Temperature can be a significant factor affecting hydrolysis of organic compounds in ground water. For example, hydrolysis rate constants are commonly reported for a temperature of 25°C. For carbon tetrachloride this would suggest a hydrolysis half-life of about 40 years. However, more typical average temperatures for ground water are 15 to 17°C, which result in half-lives of around 140 to 190 years when the Arrhenius equation is used to correct for the temperature difference.

Many classes of organic compounds hydrolyze in aqueous solutions, whereas other classes are resistant to hydrolysis. Washington (1995 — footnote 6) provides hydrolysis rate constants for many VOCs. Table 3.4 summarizes organic functional groups that are potentially susceptible to hydrolysis and those that are generally resistant.

3.3.3 Oxidation–Reduction

Along with sorption, oxidation–reduction (redox) processes are probably the most significant transformation reactions affecting contaminants in the subsurface. Abiotic and biotic redox reactions strongly affect the solubility and mobility of heavy metals. Biologically mediated redox reactions are able to transform most organic contaminants.

Oxidation–reduction (redox) reactions involve the loss of electrons and increase in oxidation number (oxidation) by one substance or system, with an associated gain of electrons and decrease in oxidation number (reduction) by another substance or system. Thus, for every oxidation, there must be a reduction. The *oxidation number* of an atom represents the hypothetical charge an atom would have if the ion or molecule were to dissociate. The oxidation number is normally expressed as a roman numeral, as in Fe(II) and Fe(III). In these cases, the oxidation number is the same numerically as the ionic charges of the ions (Fe⁺² and Fe⁺³).

Since redox reactions involve the transfer of electrons, the intensity of redox reactions is measured by equilibrium electrode potential differences, termed Eh (redox potential). Highly oxidizing conditions in the environment will have an equilibrium potential Eh of about +800 millivolts (mV); highly reducing conditions, an Eh of about –400 mV. Eh as an environmental factor is discussed in more detail in Section 3.4.2. Eh is difficult to measure accurately, and ground-water systems are often out of equilibrium with respect to redox reactions. Consequently, the Eh of a chemical system indicates the types of redox reactions that may occur, rather than predicts the specific reactions that will occur. Inorganic chemical systems tend to have redox

⁸ Scrivner, N.C., K.E. Bennet, R.A. Pease, A. Kopatsis, S.J. Sanders, D.M. Clark, and M. Rafal. 1986. Chemical Fate of Injected Wastes. In: Proceedings of the International Symposium on Subsurface Injection of Liquid Wastes, National Water Well Association, Dublin, OH, pp. 560–609. (A summary of this paper with the same title was published the same year in Ground Water Monitoring Review 6(3):53–58.)

Table 3.4 Susceptibility of Organic Functional Groups to Hydrolysis

Potentially Susceptible	Generally Resistant ^a
Alkyl halides	Alkanes
Amides	Alkenes
Amines	Alkynes
Carbamates	Benzenes/biphenyls
Carboxylic acid esters	Polycyclic aromatic hydrocarbons
Epoxides	Heterocyclic polycyclic aromatic hydrocarbons
Nitriles	
Phosphonic acid esters	Halogenated aromatics/PCBs
Phosphoric acid esters	Dieldrin/aldrin and related halogenated hydrocarbon pesticides
Sulfonic acid esters	Aromatic nitro compounds
Sulfuric acid esters	Aromatic amines
	Alcohols
	Phenols
	Glycols
	Ethers
	Aldehydes
	Ketones
	Carboxylic acids
	Sulfonic acids

^a Multifunctional organic compounds in these categories may be hydrolytically reactive if they contain other functional group(s) that are hydrolyzable.

Source: Boulding (1990), after Guswa et al. (1984).

reactions that are irreversible, but many reactions can be reversed with biological mediation. In many ways, therefore, oxidation–reduction equilibria are analogous to acid–base equilibria.

Redox Reactions Involving Simple Hydrocarbons. The simplest example of an oxidation reaction of an organic compound is the transformation of a methane to carbon dioxide and water in the presence of oxygen:



This type of reaction is called *aerobic respiration*, and without biological mediation it is irreversible. In ground water, aerobic respiration depletes dissolved oxygen, and unless a continual supply of fresh oxygen is available, a sequence of reducing reactions begins.

Table 3.5 shows the sequence of reducing reactions involving formaldehyde that will occur after oxygen is depleted in a closed ground-water system (i.e., in which there is no source of oxygen replenishment). The reactions shown in the table are not stoichiometrically correct. Anthropogenic organic chemicals can also be reduced abiotically under anaerobic conditions (Macalady et al., 1986).⁹

Redox Reactions Involving Complex Organic Compounds. Oxidation reactions involving cyclic hydrocarbons and hydrocarbon derivatives are often more complex than those involving simple hydrocarbons. It is not always obvious how to classify these chemical reactions in redox terms. Organic redox reactions most often involve the transfer of electrons via the transfer of functional groups. Oxidation frequently involves a gain in oxygen and a loss in hydrogen atoms, whereas reduction involves the reverse process. Organic functional groups can be classified in order of increasing oxidation state to facilitate the classification of reactions as either oxidation or reduction. Table 3.6 summarizes relative formal oxidation states of several major functional groups. A functional group is considered to be oxidized if its principal atom is converted to a higher

⁹Macalady, D.L., P.G. Tratnyek, and T.J. Grundl. 1986. Abiotic Reduction Reactions of Anthropogenic Organic Chemicals in Anaerobic Systems. *Journal of Contaminant Hydrology* 1:1–28.

Table 3.5 Redox Reactions in a Closed Ground Water System

Reaction	Equation
1. Aerobic respiration	$\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$
2. Denitrification	$\text{CH}_2\text{O} + \text{Nitrate } (\text{NO}_3^-) = \text{Nitrogen} + \text{CO}_2 + \text{H}_2\text{O}$
3. Mn(IV) reduction	$\text{CH}_2\text{O} + \text{MnO}_2 = \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$
4. Fe(III) reduction	$\text{CH}_2\text{O} + \text{H}^+ + \text{Fe}(\text{OH})_3 = \text{Fe}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$
5. Sulfate reduction	$\text{CH}_2\text{O} + \text{Sulfate } (\text{SO}_4^{2-}) + \text{H}^+ = \text{HS}^- + \text{CO}_2 + \text{H}_2\text{O}$
6. Methane fermentation	$\text{CH}_2\text{O} + \text{CO}_2 = \text{Methane } (\text{CH}_4) + \text{CO}_2$
7. Nitrogen fixation	$\text{CH}_2\text{O} + \text{H}_2\text{O} + \text{N}_2 + \text{H}^+ = \text{Ammonia } (\text{NH}_4) + \text{CO}_2$

Note: Equations are not stoichiometrically balanced. Reactions will tend to go to completion at equilibrium in sequence from top to bottom.

Source: Boulding (1990), after Champ et al. (1979).

Table 3.6 Relative Oxidation States of Organic Functional Groups

Functional Group		Increasing Oxidation State		
Least Oxidized		Most Oxidized		
RH	ROH	RC(O)R	RCOOH	CO ₂
	RCI	(R) ₂ CCl ₂	RC(O)NH ₂	CCl ₄
	RNH ₂		RCCl ₃	
	C=C	—C—C—		
−4	−2	0	+2	+4

Source: Boulding (1990), after Valentine (1986).

Table 3.7 Susceptibility of Organic Compounds to Oxidation in Water

Most Susceptible	Least Susceptible
Phenols	Alkenes
Aromatic amines	Haloalkanes
Olefins and dienes (electron-rich)	Alcohols
Alkyl sulfides	Esters
Enamines	Ketones

Source: Boulding (1990), after Mill (1980).

oxidation state. Similarly, reduction is defined by conversion of the principal atom within a group to a lower oxidation state.

Table 3.7 lists some organic compounds according to their susceptibility to oxidation. In general, the importance of chemical redox reactions involving organic compounds in the soil and water environment is not well documented (Valentine, 1986).¹⁰ In anaerobic environments, reduction of chemicals by both biological and nonbiological processes can occur. Reduction of organochlorine compounds (such as DDT and toxaphene), where a chlorine atom is replaced by a hydrogen atom, is an example of this type of reaction.

3.3.4 Biotransformation

Biotransformation is the alteration of a compound due to the influence of living organisms. It is one of the most prevalent processes causing the breakdown of organic compounds in the subsurface. *Biodegradation* is a more specific term used to describe the biologically mediated change of a chemical into simpler products, although the simpler daughter products may be as

¹⁰ Valentine, R.L. 1986. Nonbiological Transformation. In: Vadose Zone Modeling of Organic Pollutants, S.C. Hern and S.M. Melancon (eds.), Lewis Publishers, Chelsea, MI, pp. 223–243.

toxic or more toxic than the original compounds. For example, anaerobic biotransformation of tetra- and trichloroethylene yields equally toxic and more persistent dichlorethenes and vinyl chloride (Wood et al., 1985).¹¹

Mineralization is the complete conversion of an organic compound to its inorganic constituents (primarily water and carbon dioxide). This generally results in complete detoxification unless one of the products is of environmental concern, such as nitrate or sulfide under certain conditions. *Cometabolism* is the conversion by a microorganism of an organic compound to another compound without the microorganism using the compound as a nutrient for growth (Alexander, 1981).¹² *Cooxidation* is a similar term that is applied to oxidation of non-growth-producing hydrocarbons in the presence of growth-stimulating hydrocarbons acting as cosubstrates (Perry, 1979).¹³

Almost all of the specific chemical reactions involved in biotransformation can be classified as either oxidation–reduction, hydrolysis, or conjugative. Biotic *oxidation–reduction* reactions are broadly classified as *aerobic* (taking place in the presence of oxygen) and *anaerobic* (taking place without oxygen). See [Section 3.5.2](#) for additional discussion of these types of reactions. *Hydrolysis* reactions involve chemical reactions with water that may be biologically mediated. Goring et al. (1975) identified 26 oxidative, 7 reductive, and 14 hydrolytic transformations of pesticides.¹⁴ *Conjugation* involves the addition of functional groups or a hydrocarbon moiety to an organic molecule or inorganic species. For example, conjugation occurs when microbial processes transform inorganic mercury into dimethyl mercury.

3.3.5 Other Transformation Processes

Polymerization is a process by which large molecules (polymers) are formed by bonding together many smaller molecules. Polymerization of amino acids to peptides catalyzed by clay surfaces has been observed to increase sorption of amino acids 1000 times that expected for amino acids alone (Degens and Matheja, 1971).¹⁵ Sorption of phenol and benzene as a result of polymerization on smectite clay surfaces has been observed in the laboratory (Mortland and Halloran, 1976).¹⁶ Polymerization is probably not a major process affecting contaminants in near-surface ground-water systems.

Thermal degradation is a process by which compounds undergo structural changes in response to heat, leading to the formation of simpler species. For example, many organophosphorus esters isomerize under the influence of heat to break down to component molecules (Crosby, 1973/T4.5). In near-surface ground-water systems, thermal degradation is unlikely to be a significant process, but it may need to be considered in relation to deep-well injection of hazardous wastes.

The rates of many transformation reactions can increase in the presence of a *catalyst*, which itself remains unchanged in quantity and chemical composition when the reaction has been completed. Although the catalyst itself is not transformed, the catalytic process causes transformation by speeding up reactions that would occur naturally, or by promoting reactions that would not occur in the absence of the catalyst. For example, metal ions catalyze the hydrolysis and oxidation reactions in biochemical systems (Martell, 1971 — footnote 5), and clays catalyze numerous acid–base and redox reactions involving organic compounds (Laszlo, 1987).¹⁷

¹¹ Wood, P.R., R.F. Lang, and I.L. Payan. 1985. Anaerobic Transformation, Transport, and Removal of Volatile Chlorinated Organics in Ground Water. In: Ground Water Quality, C.H. Ward, W. Giger, and P.L. McCarty, (eds.), Wiley Interscience, New York, pp. 493–511.

¹² Alexander, M. 1981. Biodegradation of Chemicals of Environmental Concern. *Science* 211:132–138.

¹³ Perry, J.J. 1979. Microbial Cooxidations Involving Hydrocarbons. *Microbiology Review* 43(1):59–72.

¹⁴ Goring, C.A.I., D.A. Laskowski, J.W. Hamaker, and R.W. Meikle. 1975. Principles of Pesticide Degradation in Soil. In: Environmental Dynamics of Pesticides, R. Haque and V.H. Freed (eds.), Plenum Press, New York, pp. 135–172.

¹⁵ Degens, E.T. and J. Matheja. 1971. Formation of Organic Polymers on Minerals and Vice Versa. In: Organic Compounds in Aquatic Environments, S.D. Faust and J.V. Hunter (eds.), Marcel Dekker, New York, pp. 29–41.

¹⁶ Mortland, M.M. and L.J. Halloran. 1976. Polymerization of Aromatic Molecules on Smectite. *Soil Science Society of America Journal* 40:367–370.

¹⁷ Laszlo, P. 1987. Chemical Reactions on Clays. *Science* 235:1473–1477.

3.4 SUBSURFACE ENVIRONMENTAL PARAMETERS

The type and outcome of chemical reactions that will occur when contaminants reach the subsurface depend on the chemical characteristics of the contaminant and the environmental conditions that exist in the vadose and saturated zones. Six major environmental parameters of the subsurface must be considered when evaluating the fate of contaminants: (1) pH, (2) Eh, (3) salinity, (4) reservoir matrix, (5) temperature, and (6) pressure. The first four are chemical properties or measures of chemical properties of a system and provide information on what types of chemical reactions may occur and how the reactions might be expected to proceed. The last two, temperature and pressure, are physical properties of the system that primarily influence the rate of chemical reactions.

3.4.1 pH

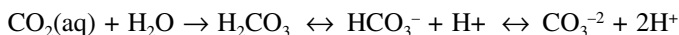
The symbol *pH* stands for the negative logarithm of the hydronium ion concentration [H_3O^+] and is a convenient way of expressing the very low concentrations of H_3O^+ that are present in aqueous solutions. In chemical reactions, the term H^+ is often used instead of H_3O^+ . Pure water has a pH of 7.0. Solutions of pH less than 7.0 are acidic, and those of pH greater than 7.0 are basic. Acid–base reactions (Section 3.2.1) determine the pH of a solution at equilibrium.

The pH of a system greatly influences what chemical processes will occur in the subsurface environment. Directly or indirectly, pH also affects most of the other environmental factors that are discussed in this chapter. Table 3.8 summarizes the significance and some major effects of changes in pH on chemical processes and environmental factors in the subsurface.

Very small changes in acidity greatly affect chemical reactions and the form of chemical species in solution. Figure 3.2 illustrates how pH influences the distribution of molecular and ionic species of cadmium, mercury, and lead, respectively.

Buffer capacity is a measure of how much the pH changes when a strong acid or base is added to a solution. A highly buffered solution will show little change in pH with the addition of a strong acid or base. Conversely, the pH of a solution with low buffering capacity will change rapidly if an acid or base is added to that solution. Weak acids or bases buffer a solution, and the higher their concentration in solution, the greater the buffering capacity. *Alkalinity*, which is usually expressed in calcium carbonate equivalents required to neutralize acid to a specified pH, is a measure of the buffering capacity of a solution.

Acid–base equilibrium reactions of buffers act to either add or remove hydrogen ions to or from the solution so as to maintain a nearly constant equilibrium concentration of H^+ . For example, carbon dioxide acts as a buffer when it dissolves in water to form carbonic acid, which then dissociates to carbonate and bicarbonate ions according to the following formula:



(carbonic acid) (carbonate) (bicarbonate)

At equilibrium, the concentration of H^+ will remain constant. When a strong acid (represented by H^+) is introduced into solution, the concentration of H^+ is increased. The buffer compensates by reacting with the excess H^+ ions, moving the direction of the above reaction to the left. By combining with bicarbonate and carbonate ions to form the nonionic carbonic acid, equilibrium is reestablished at a pH nearly the same as that existing before the acid was added. The buffer capacity in this case is determined by the total concentration of carbonate and bicarbonate ions. When carbonate or bicarbonate ions are no longer available to combine with excess H^+ ions, the buffer capacity has been exceeded and pH will decrease rapidly upon addition of further acid.

Table 3.8 Effects of pH on Subsurface Geochemical Processes and Other Environmental Factors

Process/Factor	pH Effect
Distribution Process	
Acid–base	Measures acid–base reactions. Strong acids (bases) will tend to change pH; weak acids (bases) will buffer solutions to minimize pH changes.
Sorption	Strongly influences sorption, because hydrogen ions play an active role in both chemical and physical bonding processes. Mobility of heavy metals is strongly influenced by pH. Adsorption rates of organics may also be pH dependent.
Precipitation–dissolution	Strongly influences precipitation–dissolution reactions. Mixing of solutions with different pH values often results in precipitation reactions. See also reservoir matrix below.
Transformation Process	
Complexation	Strongly influences positions of equilibria involving complex ions and metal chelate formation.
Hydrolysis	Strongly influences rates of hydrolysis. Hydrolysis of aliphatic and alkyl halides optimum at neutral to basic conditions. Other hydrolysis reactions tend to be faster at either high or low pH.
Oxidation–reduction	Redox systems generally become more reducing with increasing pH.
Environmental Factor	
Biotransformation	In combination with Eh, strongly influences the types of bacteria that will be present. High- to medium-pH, low-Eh environments will generally restrict bacterial populations to sulfate reducers and heterotrophic anaerobes. In reducing conditions, pH strongly affects whether methanogenic or sulfate-reducing bacteria predominate.
Eh	Increasing pH generally lowers Eh.
Salinity	pH-induced dissolution increases salinity; pH-induced precipitation decreases salinity.
Reservoir matrix	Acidic solutions tend to dissolve carbonates and clays; highly alkaline solutions tend to dissolve silica and clays. Greater pH generally increases cation exchange capacity of clays.
Temperature	pH-driven exothermic (heat-releasing) reactions will increase fluid temperature; pH-driven endothermic (heat-consuming) reactions will decrease fluid temperature.
Pressure	Will not influence pressure unless pH-induced reactions result in a significant change in the volume of reaction products.

Source: Boulding (1990).

3.4.2 Eh and Other Redox Indicators

The term *Eh*, which is the *oxidation–reduction potential* (often referred to as *redox potential*), is an expression of the tendency of a reversible redox system to be oxidized or reduced. It is especially significant in its influence on biotransformation processes (see [Section 3.5.4](#)). The energy of oxidation (electron-escaping tendency) present in a reversible oxidation–reduction system (in volts or millivolts) is measured as the potential difference between a standard hydrogen electrode and the system being measured. Large positive values (up to about +800 mV) indicate a strong oxidizing tendency, and large negative values (down to about –500 mV) indicate a strong reducing tendency. Eh values of +200 mV and lower are used as indicators of reducing conditions in near-surface soils and sediments (Ponnamperuma, 1972).¹⁸ Eh ranges for the various redox reactions listed in Table 3.5 are denitrification (+250 to +100 mV), Fe/Mn reduction (+100 to 0 mV), sulfate reduction (0 to –200 mV), and methane fermentation/nitrogen fixation (–200 mV and lower). [Figure 3.3](#) shows typical Eh–pH ranges of natural surface and subsurface aquatic environments.

As long as dissolved oxygen is present in ground water, aerobic respiration should be possible ([Section 3.3.3](#)). Typically, the bulk of dissolved oxygen in recharge water is consumed in the soil and unsaturated zone by microbial respiration and the decomposition of organic matter. Dissolved

¹⁸ Ponnamperuma, F.N. 1972. The Chemistry of Submerged Soils. *Advances in Agronomy* 24:29–98.

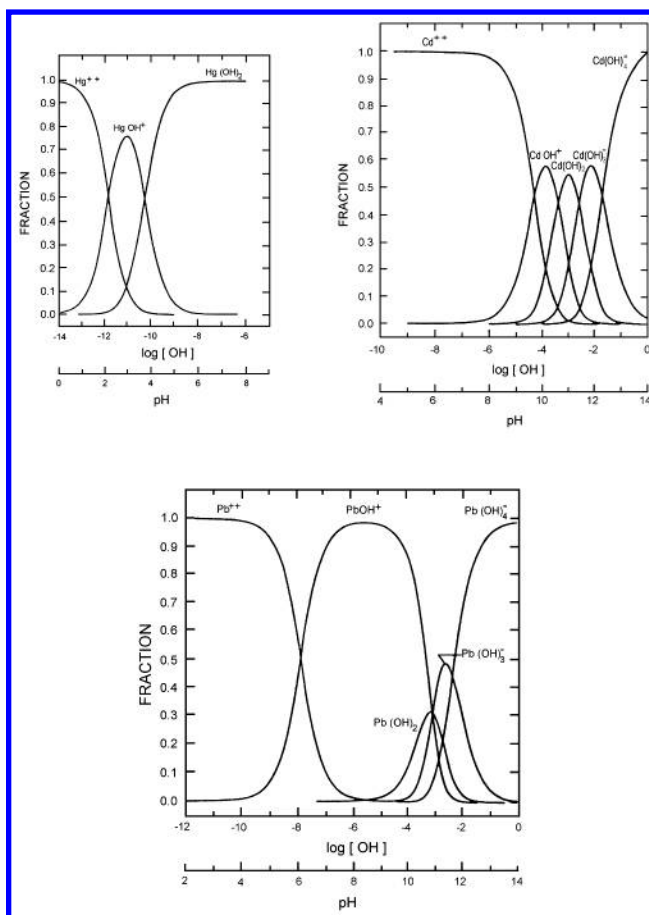


Figure 3.2 Distribution of molecular and ionic species of divalent cadmium, mercury, and lead at different pH values (Boulding, 1990, after Hahne and Kroontje, 1973).

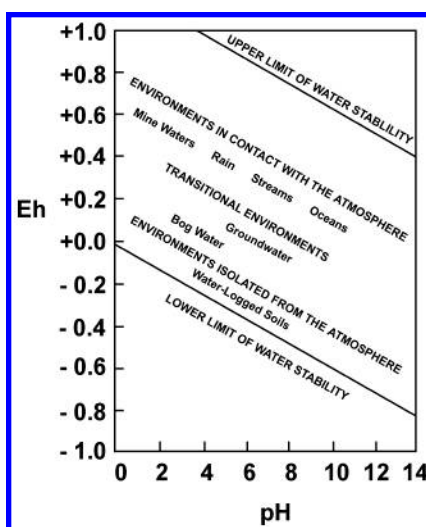


Figure 3.3 pH-Eh diagram showing the ranges of various aquatic environments (Johnson et al., 1989).

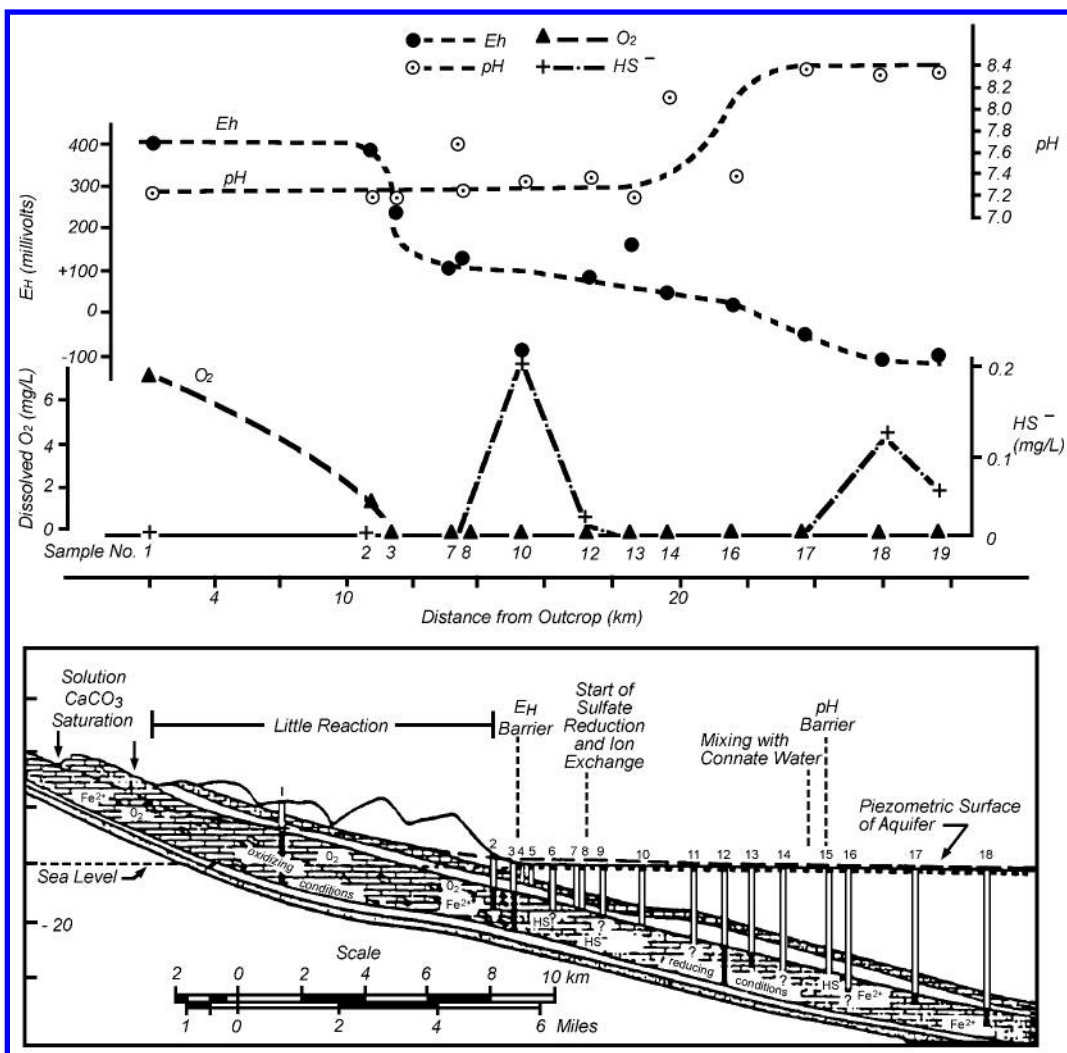


Figure 3.4 Horizontal gradients in uncontaminated oxidation–reduction conditions (Boulding and Barcelona, 1991b, after Champ et al., 1979).

oxygen concentration may be expected to be highest in ground water near recharge zones. In general, redox conditions will become progressively more reducing as water travels into deeper aquifers. Figure 3.4 illustrates this process. Sand and gravel aquifers will tend to have higher levels of dissolved oxygen than silty and clayey materials. Winograd and Robertson (1982)¹⁹ reported dissolved oxygen values from 2 to 8 mg/l from a variety of deep (100 to 1000 m) aquifers, so reducing conditions should not always be assumed on the basis of depth or distance from the recharge areas alone.

The Eh of connate waters (i.e., water entrapped in the interstices of sediment at the time of deposition) typically ranges from 0 to –200 mV (Baas-Becking et al., 1960).²⁰ Barcelona et al. (1989)²¹ provide a good review of the literature on horizontal and vertical gradients in subsurface oxidation–reduction conditions at both site and regional scales.

¹⁹ Winograd, I.J. and F.N. Robertson. 1982. Deep oxygenated ground water: anomaly or common occurrence? *Science* 216:1227–1229.

²⁰ Baas-Becking, L.G.M., I.R. Kaplan, and D. Moore. 1960. Limits of the Natural Environment in Terms of pH and Oxidation-Reduction Potentials. *Journal of Geology* 68(3):243–284.

²¹ Barcelona, M.J., T.R. Holm, M.R. Schock, and G.K. George. 1989. Spatial and temporal gradients in aquifer oxidation-reduction conditions. *Water Resources Res.* 25(5):991–1003.

Several measures of organic pollutant loading to waters indicate the redox status of a system: (1) biochemical oxygen demand (BOD), (2) chemical oxygen demand (COD), (3) total organic carbon (TOC), (4) dissolved organic carbon (DOC), and (5) suspended organic carbon (SOC).²² When high values exist for any of these parameters, oxygen may be rapidly depleted in ground waters and reducing conditions will develop. BOD and COD were designed to measure oxygen consumption during the microbial degradation of municipal sewage. They are, however, only semiquantitative indicators of organic loading because measurement procedures for these parameters have no particularly direct geochemical significance. DOC and SOC are the most useful parameters for geochemical interpretation.²³

Introduction of organic contaminants usually reduces Eh because microbiological activity rapidly depletes available oxygen unless toxic effects inhibit growth (see [Section 3.5.3](#)). On the other hand, artificial recharge of ground water by injection of treated wastes tends to create aerobic conditions in the immediate vicinity of injection wells. For example, Ragone et al. (1973)²⁴ observed a change from reducing to oxidizing conditions when tertiary-treated sewage (reclaimed water) was injected into the Magothy aquifer, Long Island, NY, at a depth of 400 ft. The reclaimed water had 6.6 mg/l dissolved oxygen compared to no detectable dissolved oxygen in the formation water.

3.4.3 Salinity

Salinity is defined as the concentration of total dissolved solids (TDS) in a solution, usually expressed in milligrams per liter. The TDS concentration in water is usually determined from the weight of the dry residue remaining after the volatile portion of the original solution evaporates. Ground water can be classified into four salinity classes:

- Slightly saline (1000 to 3000 mg/l)
- Moderately saline (3000 to 10,000 mg/l)
- Very saline (10,000 to 35,000 mg/l)
- Brine (more than 35,000 mg/l)

Seawater lies in the upper range of very saline water (about 34,000 mg/l); deep sedimentary basins may have salinities as high as 300,000 mg/l (Kreitler, 1986).²⁵ Most contamination of near-surface aquifers involves slightly to moderately saline waters. Pumping of ground water where denser seawater is present at greater depths may contaminate an aquifer by saltwater intrusion.

Solutions of substances that are good conductors of electricity are called *electrolytes*. For example, sodium chloride, a major constituent of seawater, is a strong electrolyte. Most salts, as well as strong acids and bases, are strong electrolytes because they remain in solution primarily in ionic (charged) forms. Weak acids and bases are weak electrolytes because they do not fully dissociate into ionic species in solution. Pure water is a nonconductor of electricity. The high concentration of ions in very saline and briny waters creates more complex thermodynamic properties of the fluid, and hence makes geochemical modeling more difficult. In evaluating the geochemistry of near-surface aquifers, these kinds of interactions often require special consideration.

The electrical conductivity of solutions is measured as *specific conductance*, usually expressed as microsiemens per centimeter ($\mu\text{S}/\text{cm}$ — SI units) or micromhos per centimeter ($\mu\text{mhos}/\text{cm}$) at

²² SOC may also be used as an abbreviation for soil organic carbon. The meaning of the abbreviation should usually be evident from the context of the discussion.

²³ Malcolm, R.L. and J.A. Leenheer. 1973. The Usefulness of Organic Carbon Parameters in Water Quality Investigations. In: Proceedings of the Institute of Environmental Sciences 1973 Annual Meeting, Anaheim, CA, April 1–6, pp. 336–340.

²⁴ Ragone, S.E., J. Vecchioli, and H.F.H. Ku. 1973. Short-term effect of injection of tertiary-treated sewage on iron concentration of water in Magothy Aquifer, Bay Park, New York, in Symp. on Underground Waste Management and Artificial Recharge, J. Braunstein, Ed., Pub. No. 110, Intl. Assoc. Hydrological Sci., pp. 273–290.

²⁵ Kreitler, C.W. 1986. Hydrogeology of Sedimentary Basins as It Relates to Deep-Well Injection of Chemical Wastes. In: Proceedings of the International Symposium on Subsurface Injection of Liquid Wastes, National Water Well Association, Dublin, OH, pp. 398–416.

Table 3.9 Half-Lives of Different Forms of Organic Matter

Form	Half-Life (Years)
Nonhumic Substances	
Decomposable plant material	0.17
Living biomass	1.7
Woody plant material	2.3
Humic Substances	
Physically stabilized	50
Chemically stabilized	1000

Source: Boulding (1990), after Jenkinson and Raynor (1977).

25°C. Seawater has a specific conductance of about 50,000 $\mu\text{mhos/cm}$. Specific conductance shows a high correlation with salinity at low to moderate TDS levels, and is thus a very useful parameter to measure in the field characterization of ground-water systems.

3.4.4 Soil and Aquifer Matrix

The solid matrix of an aquifer is typically unconsolidated or lithified sediments (see Sections 1.1.3 and 1.1.4). The reactions that take place when a contaminant enters an aquifer are largely determined by the physical and chemical properties of the aquifer solids. The most important physical properties of subsurface materials in relation to geochemical interactions are *texture* (Section 1.1.2) and *specific surface area*. The most important chemical property is *mineralogy*, which is defined by the types and proportions of minerals present (Section 1.1.1). *Organic matter*, the most geochemically reactive portion of the solid phase in the subsurface, is the focus of this section.

There are two major classes of organic matter: (1) nonhumic substances, which are largely water soluble, of low molecular weight, and susceptible to microbial metabolism, and (2) humic substances, which are largely water insoluble, of high molecular weight, and relatively resistant to further microbial degradation. Table 3.9 shows further subdivisions of these classes and estimated half-lives for decomposition.

Humic substances consist of an operationally defined class of biogenic, refractory, yellow–black organic substances that occur in all terrestrial and aquatic environments. Although they have been studied by scientists for about 200 years, no fundamental, or even generally accepted, understanding of the nature, origin, and geochemical role of humic substances has been developed (Aiken et al., 1985).²⁶

Humic substances are classified into three major groups: (1) humic acids (insoluble at a pH of <2, soluble at higher pH), (2) fulvic acids (soluble under all pH conditions), and (3) humins (insoluble residue). Humic acids have colloidal properties, and their structure is based primarily on six-membered aromatic and heterocyclic rings, which may include benzene, naphthalene, and anthracene (Manaskaya and Drozdova, 1968/T3.12).

The mobility and toxicity of contaminants in the subsurface may be affected by a number of important chemical properties and characteristics of humic substances:

- High sorption capacity for metals and organic pollutants
- Ability to readily form complexes with heavy metals
- Ability to incorporate organic pollutants with similar structures to the building blocks of humus (such as chlorinated phenols, naphtholic compounds, and halogenated anilines) when humus forms
- Ability to solubilize organic compounds that are otherwise water insoluble

²⁶ Aiken, G.R., D.M. McKnight, R.L. Wershaw, and P. MacCarthy. 1985. An Introduction to Humic Substances in Soil, Sediment, and Water. In: Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization, G.R. Aiken, D.M. McKnight, R.L. Wershaw, and P. MacCarthy (eds.), John Wiley & Sons, New York, pp. 1–9.

- Ability to increase hydrolysis reactions as a catalyst or, conversely, to slow the rate of hydrolysis reactions by sorption
- Ability to affect the rate and pathways of oxidation–reduction reactions

Humic substances dissolved in ground water are important as substrates for microorganisms and may be geochemically significant as complexing agents. The amounts of dissolved organic matter in ground waters are sufficient to support small but diverse populations of microorganisms that may be able to adapt and degrade organic contaminants (see [Section 3.5](#)). Complexation of heavy metals by humic substances will generally be limited by the low dissolved organic carbon content of most ground waters.

Except as noted below, most ground waters contain less than 1 mg of dissolved organic carbon per liter. Thurman (1985),²⁷ using data primarily from Leenheer et al. (1974),²⁸ reports the following median concentrations of organic carbon in various types of aquifers: sand and gravel, limestone, and sandstone, 0.7 mg/l; igneous, 0.5 mg/l; oil shales, 3.0 mg/l; organically rich recharge waters, 10.0 mg/l; and petroleum-associated waters, 100.0 mg/l. Dissolved organic carbon represents typically less than 1% of the total organic carbon in an aquifer system. The bulk of the carbon in the aquifer solids remains uncharacterized.

3.4.5 Temperature and Pressure

Temperature and pressure are environmental factors that primarily influence the rate of chemical reactions. *Temperature* is measured in degrees using three main temperature scales: Fahrenheit (°F), Centigrade (°C), and Kelvin (°K). *Pressure* is measured in a variety of units, the most common scales being bars, atmospheres (atm), megapascals (MPa), and pounds per square inch (psi). Both temperature and pressure increase with depth below the earth's surface. Consequently, temperatures and pressures in deep aquifers are significantly higher than those encountered in near-surface aquifers and should receive particular attention when assessing the geochemical fate of deep-well-injected wastes.

The rates of most acid–base and dissolution reactions increase as temperature increases. Increased temperature often increases the rate of redox reactions as well. However, the exact effect is difficult to predict because the interactions between competing reactions may offset the effect of increased temperature (Valentine, 1986 — footnote 10).

3.5 MICROBIAL ECOLOGY OF THE SUBSURFACE

3.5.1 Classification of Microorganisms

Microorganisms are by far the most significant group of organisms involved in biotransformation. Numerous biochemical pathways for degradation are present in this group because high rates of reproduction and mutation contribute to a great diversity of species, adapted strains, and enzyme systems.

Microorganisms fall into three main groups: (1) *bacteria* (single-cell organisms), (2) *actinomyces* (filamentous unicellular organisms with characteristics of both bacteria and fungi), and (3) *fungi*, such as mold and yeasts. Bacteria are dominant in the saturated zone; actinomycetes and fungi may be very active in the soil rooting zone.

²⁷ Thurman, E.M. 1985. Humic Substance in Groundwater. In: Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization, G.R. Aiken, D.M. McKnight, R.L. Wershaw, and P. MacCarthy (eds.), John Wiley & Sons, New York, pp. 87–103.

²⁸ Leenheer, J.A., R.L. Malcolm, P.W. McKinley, and L.A. Eccles. 1974. Occurrence of Dissolved Organic Carbon in Selected Groundwater Samples in the United States. *Journal of Research of the U.S. Geological Survey* 2:361–369.

Bacteria may be classified as either *heterotrophic*, requiring organic matter for growth, or *autotrophic*, capable of growth on inorganic carbon (carbon dioxide). They may also be *aerobic*, requiring oxygen for respiration, or *anaerobic*, not requiring oxygen for respiration.

Anaerobic microorganisms may be either obligately anaerobic or facultatively anaerobic. Oxygen is toxic to *obligate* microorganisms, whereas *facultative* microorganisms can live with or without oxygen. Groups of anaerobic microorganisms that may be important in the degradation of contaminants in the subsurface include:

- *Fermenters*, which degrade complex organic compounds to simpler organic compounds and may also mineralize organic compounds to hydrogen and carbon dioxide. Fermenters called *acetogens* produce acetate from biomonomers (sugars, amino acids, peptides, and alcohols), which can then be used by sulfate-reducing and methanogenic bacteria. Acetogens are particularly important in this group.
- *Denitrifiers*, which mineralize an appropriate carbon source in the presence of nitrate to form nitrogen, carbon dioxide, and water (see Equation 2, Table 3.5).
- *Sulfate reducers*, which can mineralize an appropriate carbon source in the presence of sulfate and hydrogen to form hydrogen sulfide, carbon dioxide, and water (see Equation 5, Table 3.5).
- *Methanogens*, which can mineralize an appropriate carbon source (for example, acetate or methylated amines) to form methane and carbon dioxide (see Equation 6, Table 3.5). Methanogens may also use carbon dioxide as a growth source in the presence of hydrogen (H_2), producing methane as a by-product.

Iron- and manganese-reducing bacteria are another important group of bacteria that may significantly affect geochemical reactions in ground water (Ehrlich, 1987; Ghiorse, 1988; Lovely, 1987).²⁹ However, the role that these bacteria may have in degrading organic contaminants has received less attention by researchers than denitrification and methane fermentation. Iron-reducing bacteria have been observed to degrade aromatic hydrocarbons in ground water from a crude oil spill (Lovely et al., 1989).³⁰ Petrovskis et al. (1995)³¹ observed both biotic and abiotic degradation of carbon tetrachloride under iron-reducing conditions.

3.5.2 Natural Biological Activity in the Subsurface

Microorganisms are ubiquitous in the shallow and deep subsurface. Microorganisms have adapted to live in essentially the complete range of environmental conditions that exist on and below the earth's surface. They have been observed at pressures up to 25,000 psi, temperatures up to 100°C, and salt concentrations up to 300,000 mg/l (Kuznetsov et al., 1963/T3.12). In recent years thermophilic bacteria have been isolated from marine and terrestrial geothermal sites whose optimum temperature for growth approaches, and in some cases exceeds, 100°C (Borman, 1991).³² Ghiorse and Wilson (1988/T3.12) summarized data on studies of the types, abundance, and activities of microorganisms in subsurface materials in pristine sites. Depths of ground water sampled in these studies ranged from 1.2 to 1752 m, and included a wide diversity of geologic materials (unconsolidated sands, gravels, clays, sandstone, and limestone). In all instances, evidence of

²⁹ Ehrlich, H.L. 1987. Manganese Oxide Reduction as a Form of Anaerobic Respiration. *Geomicrobiology Journal* 5:423–429. Ghiorse, W.C. 1988. Microbial Reduction of Manganese and Iron. In: *Biology of Anaerobic Microorganisms*, A.J.B. Zehnder (ed.), John Wiley & Sons, New York, pp. 305–331. Lovely, D.R. 1987. Organic Mineralization with the Reduction of Ferric Iron: A Review. *Geomicrobiology Journal* 5:375–399.

³⁰ Lovely, D.R., M.J. Baedeker, D.J. Lonergan, I.M. Cozzarelli, E.J.P. Phillips, and D.I. Siegel. 1989. Oxidation of Aromatic Contaminants Coupled to Microbial Iron Reduction. *Nature* 339:297–300.

³¹ Petrovskis, E.A., T.M. Vogel, D.A. Saffarini, K.H. Nealson, and P. Adriaens. 1995. Transformation of Tetrachloromethane by *Shewanella putrefaciens* MR.1. In: *Bioremediation of Chlorinated Solvents*, R.E. Hinchee, A. Leeson, and L. Semprini, Eds., Battelle Press, Columbus, OH, pp. 61–67.

³² Borman, S. 1991. Bacteria That Flourish above 100°C Could Benefit Industrial Processing. *Chemical and Engineering News*, November 4, pp. 31–34.

microbiological activity was found at the maximum depth sampled. Typically, viable counts of microorganisms ranged from 10^3 to 10^6 viable organisms per gram.

Particle size is a major factor affecting microbiological activity in the subsurface. Messineva (1962),³³ in studies on the geological activity of bacteria in the Soviet Union, found that mineralization of organic matter by bacteria occurs most rapidly in sand–silt sediments. In clay and clay–silt sediments, the process of mineralization slows down, despite the fact that the number of bacteria in the clay sediments is considerably greater than that in sand–silt sediments. Other major environmental factors that affect subsurface microbial activity include nutrient availability, redox conditions, nutritional ecology, and surface activity of the solid matrix.

3.5.3 Aerobic vs. Anaerobic Degradation

In aerobic degradation, oxygen serves as an electron acceptor and is converted to water, releasing energy that can be used by microorganisms in the process. More energy can be obtained from this reaction (125.1 kJ) than from competing potential anaerobic reactions. Consequently, this type of reaction will predominate as long as dissolved oxygen is present in the ground water. The toxicity of oxygen to obligate anaerobes also inhibits anaerobic activity in the presence of oxygen.

Once the oxygen is depleted, anaerobic degradation reactions may follow the equilibrium sequence shown in Table 3.5 using nitrate, Mn(IV), Fe(III), sulfate, nitrate (again, if all the nitrate has not been consumed earlier in the sequence), and carbon dioxide as electron acceptors. The reaction sequence is listed in order of energy released, with nitrate reduction (denitrification) releasing the most (118.8 kJ) and methane fermentation the least (23.2 kJ). Thermodynamics thus favors bacteria that participate in higher energy reactions over lower energy reactions, as long as the higher energy electron acceptors are available. Once higher energy electron acceptors are depleted, biological activity will focus on reactions the next step down in the reaction sequence. The redox reaction sequence in Table 3.5 shows only some of the most common reactions in ground water. Zehnder and Stumm (1988)³⁴ list a total of 23 redox reactions pertinent in aquatic conditions. Electron acceptors other than the ones already mentioned include NO_2^- , S, CH_2O , CH_3OH , and HCOO^- .

Decomposition of organic matter in anaerobic environments often depends on the interaction of metabolically different bacteria. Degradation in this situation is a multistep process in which complex organic compounds are first degraded to short-chain acids by facultative bacteria (see Figure 3.5). Acetogenic bacteria degrade the acids to produce hydrogen (H_2) and acetate. H_2 , CO_2 , and acetate are termed *competitive substrates* because they can be metabolized by both methanogenic and sulfate-reducing bacteria.

Where sulfate is present, sulfate reduction will be favored over methane production. Winfrey and Zeikus (1977)³⁵ have shown that sulfate inhibits methanogenesis in freshwater sediments by altering normal carbon and electron flow during anaerobic mineralization. They proposed that sulfate reducers assume the role of methanogens in sulfate-containing sediments by metabolizing methanogenic precursors. Sulfate-reducing bacteria will outcompete methanogens for H_2 and acetate. Martens and Berner (1974)³⁶ found that methanogenesis in marine sediments is not initiated until sulfate is depleted from interstitial water. Where sulfate is absent, methanogenic bacteria will be the end stage of the biodegradation process.

³³ Messineva, M.A. 1962. The Geological Activity of Bacteria and Its Effect on Geochemical Processes. In: *Geologic Activity of Microorganisms*, S.I. Kuznetsov, Ed., Trans. Inst. Microbiol. No IX (translated from Russian), Consultants Bureau, New York, pp. 6–24.

³⁴ Zehnder, A.J.B. and W. Stumm. 1988. *Geochemistry and Biogeochemistry of Anaerobic Habitats*. In: *Biology of Anaerobic Microorganisms*, A.J.B. Zehnder, Ed., John Wiley & Sons, New York, pp. 1–38.

³⁵ Winfrey, M.R. and J.G. Zeikus. 1977. Effect of Sulfates on Carbon and Electron Flow During Microbial Methanogenesis in Freshwater Sediments. *Appl. Environ. Microbiol.* 33:275–281.

³⁶ Martens, C.S. and R.A. Berner. 1974. Methane Production in the Interstitial Waters of Sulfate-Depleted Marine Sediments. *Science* 185:1167–1169.

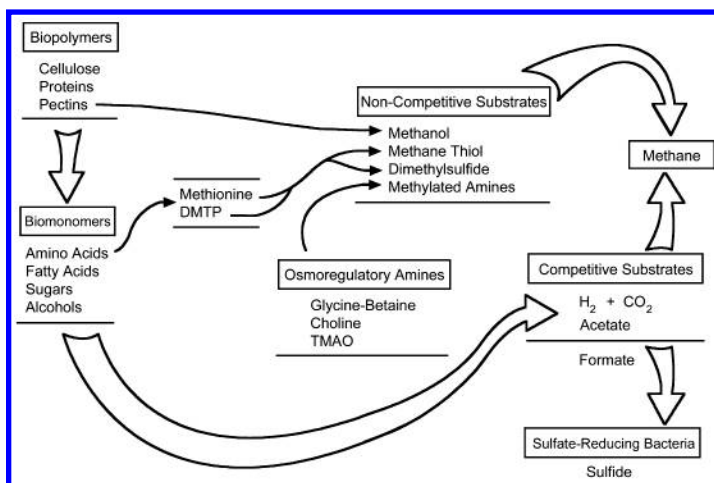


Figure 3.5 Anaerobic food web for aquatic microbial ecosystems (Oremland, 1988).

Bivalent cations may inhibit sulfate-reducing bacteria, although the reason is not understood (Kuznetsov et al., 1963/T3.12). Porter (1946/T3.12) reports the following sequence of relative inhibition of sulfate-reducing bacteria by cations: $\text{Na} < \text{K} < \text{NH}_4 < \text{Mg} < \text{Ca} < \text{Ba} < \text{Mn} < \text{Fe}^{+2} < \text{Zn} < \text{Fe}^{+3} < \text{Al} < \text{Pb} < \text{Cu} < \text{Hg} < \text{Ag}$.

Methanogenic bacteria may survive in a wide range of environmental conditions, but require more restricted conditions for optimal growth. The optimum temperature range for methane production by species in sediments of Lake Mendota, Wisconsin, measured *in vitro* was 35 to 42°C, well above the maximum *in situ* temperature of 23°C (Zeikus and Winfrey, 1976).³⁷ DiTommasso and Elkan (1973)³⁸ report that 20 to 50 µg of iron per liter are required for methane fermentation. Wolin and Miller (1987)³⁹ describe in detail the interactions between acetogenic bacteria and methanogens involved in the complete bioconversion of organic carbon to methane and carbon dioxide.

The addition of sulfate and other compounds (nitrate, nitrite, acetylene) to sediments has been shown to inhibit methanogenesis (Zeikus, 1977).⁴⁰ Cappenberg (1975)⁴¹ has suggested that the inhibition of methanogenesis by the presence of sulfates results from the production of toxic H_2S .

The inhibiting effects of sulfates on methane production would seem to indicate that sulfate reduction will take place in preference to methanogenesis as long as sulfates are present. However, the ecological significance of sulfate reducer–methanogen interrelationships is not well understood. Cappenberg (1975 — footnote 37) found that lactate metabolism by sulfate-reducing bacteria in the upper sulfate-containing sediment layers at Lake Vechten provides the main energy source for acetate-fermenting methanogens located lower in the sediment.

3.5.4 Biotransformation of Organic Contaminants

As noted in Section 3.5.2, most ground waters support a small but diverse population of microorganisms. In near-surface, pristine ground waters, aerobic bacteria will typically dominate

³⁷ Zeikus, J.G. and M. Winfrey. 1976. Temperature Limitation of Methanogenesis in Aquatic Sediments. *Applied Environmental Microbiology* 31:99–107.

³⁸ DiTommasso, A. and G.H. Elkan. 1973. Role of Bacteria in Decomposition of Injected Liquid Waste at Wilmington, North Carolina. In: *Symp. on Underground Waste Management and Artificial Recharge*, J. Braunstein (ed.), IASH Pub. No. 110, pp. 585–599.

³⁹ Wolin, M.J. and T.L. Miller. 1987. Bioconversion of Organic Carbon to CH_4 and CO_2 . *Geomicrobiology J.* 5:239–259.

⁴⁰ Zeikus, J.G. 1977. The Biology of Methanogenic Bacteria. *Bacteriology Review* 41:514–541.

⁴¹ Cappenberg, T.E. 1975. A Study of Mixed Continuous Culture of Sulfate-Reducing and Methane-Producing Bacteria. *Microbial Ecol.* 2:60–72.

Table 3.10 Redox Zones for Biotransformation of Organic Micropollutants

Increasing Distance from Pollutant Source →			
Biological Conditions			
Aerobic heterotrophic respiration	Denitrification	Sulfate respiration	Methanogenesis
Organic Pollutants Transformed			
Chlorinated benzenes	Carbon tetrachloride Bromodichloromethane	C ₁ and C ₂ Halogenated aliphatics (alkenes)	
Ethylbenzene	Dibromochloromethane		
Styrene	Bromoform		
Naphthalene			

Source: Boulding (1990), after Bouwer and McCarty (1984).

unless unusually high concentrations of dissolved organic carbon (recharge from stagnant swamps, for example) have created more reducing conditions. However, denitrifiers, sulfate reducers, and methanogens are likely to be present in low numbers. Microbiological activity in ground water is usually characterized by a dominant consortium of species favored by the predominant redox potential, with smaller numbers of other species in a quiescent state or thriving in microenvironments with differing redox potentials from the dominant one.

When a potential energy source in the form of an organic contaminant enters the water, the group most capable of utilizing the substrate at the environmental conditions existing in the aquifer will adapt and increase in population. The population of other indigenous microbes will remain small, or possibly be eliminated if the new environment is unfavorable for their survival. The microbial population will change as the favored electron acceptors are depleted.

Whether an organic contaminant will be biodegraded in the subsurface depends on (1) the existence of microorganisms capable of degrading the contaminant, and (2) environmental conditions that favor the growth of these microbes. Since different contaminants may be degraded by different microorganisms, the concept of redox zones for biotransformation of micropollutants has been proposed by Bouwer and McCarty (1984).⁴² Table 3.10 presents a hypothetical sequence for biotransformation of microcontaminants in treated sewage effluent that is injected into ground water. Any contaminants that are not degraded in their appropriate redox zone will tend to migrate unchanged once they enter subsequent zones (unless other distribution or transformation processes occur).

Where contaminants are highly concentrated (as with deep-well injection of hazardous wastes), the redox zone model shown in Table 3.10 does not work because of toxic effects. In this situation, biotransformation is restricted to a relatively narrow moving front where contaminant concentrations are low enough to prevent toxic effects, but high enough to allow significant growth of adapted microorganisms (see Figure 3.6). The sequence shown in this figure has been observed at a site in Wilmington, NC, where wastes containing organic acids, formaldehyde, and methanol were injected (Leenheer and Malcolm, 1973).⁴³

The zone of microbial activity in Figure 3.6 may also develop redox zones similar to those shown in Table 3.10, but they are likely to be reversed in order, since redox potential will be lowest where contaminant concentrations are highest. In fact, this reverse zonation is likely to exist where near-surface ground water is heavily contaminated. For example, Ehrlich et al. (1983)⁴⁴ observed

⁴² Bouwer, E.J. and P.L. McCarty. 1984. Modeling of Trace Organics Biotransformation in the Subsurface. *Ground Water* 22:433–440.

⁴³ Leenheer, J.A. and R.L. Malcolm. 1973. Case History of Subsurface Waste Injection of an Industrial Organic Waste. In: *Symposium on Underground Waste Management and Artificial Recharge*, J. Braunstein (ed.), Publication 110, International Association of Hydrological Sciences, pp. 565–584.

⁴⁴ Ehrlich, G.G., E.M. Godsy, D.F. Goerlitz, and M.F. Hult. 1983. Microbial Ecology of a Creosote-Contaminated Aquifer at St. Louis Park, Minnesota. *Dev. Ind. Microbiol.* 24:235–245.

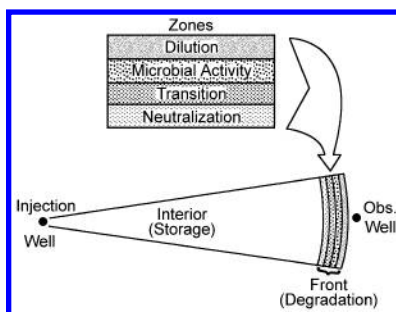


Figure 3.6 Geochemical zones with subsurface injection of concentrated toxic wastes (Boulding, 1990, after Leenheer and Malcolm, 1973).

evidence of both denitrifying and methanogenic bacteria in phenol-depleted zones of a creosote-contaminated aquifer, and concluded that the denitrifying bacteria contributed to the degradation process. Denitrifiers and iron reducers were the dominant anaerobes in contaminated wells, but methane production was highest in the wells that were most contaminated, wells just downgradient from the creosote source. Thus, the redox zones shown in Table 3.10 were reversed, with methanogenic conditions strongest close to the contaminant source, grading to denitrifying conditions farther from the site, where contaminant concentrations were lower.

Table 3.11 identifies the susceptibility of 34 types of RCRA-regulated organic compounds to biodegradation by aerobic and anaerobic respiration, fermentation, oxidation, and cooxidation.

Aerobic biotransformation of contaminants has been widely studied because one of the most common ground-water contaminants, gasoline, is composed of compounds that are readily degraded aerobically. Unpolluted near-surface aquifers typically contain enough oxygen for aerobic conditions to prevail. In general, organic contaminants are more readily degraded aerobically than anaerobically. For example, of about 90 examples of hazardous anthropogenic compounds and microorganisms that can degrade them, compiled by Kobayashi and Rittmann (1982/T4.5), less than a third involved anaerobic degradation processes. Groups most susceptible to aerobic degradation include chlorobenzenes, alkylbenzenes, phenol and alkyl phenols, chlorophenols, aliphatic hydrocarbons, and two- and three-ring polynuclear aromatic hydrocarbons. Hazardous organic compounds that are susceptible to biotransformation under anaerobic conditions include halogenated aliphatic hydrocarbons, brominated methanes, phenol and alkyl phenols, and chlorophenols.

Fifteen years ago anaerobic degradation of organic contaminants was considered to be relatively unimportant in ground water. Anaerobic biotransformation of organic contaminants has received increasing attention in recent years because of the recognition that (1) certain organic contaminants, such as many chlorinated solvents, that are not amenable to aerobic degradation can be degraded anaerobically, and (2) reducing conditions are common in the subsurface, especially where ground water is contaminated.

When considering biotransformation of toxic organic compounds in the subsurface, it is important to recognize that many degradation pathways may be possible, some of which result in toxic daughter products that may be as much, or more, of a concern than the original compound. Even if the daughter compounds are not more toxic, they may be more persistent. For example, there is a large literature on the biotransformation of carbon tetrachloride.⁴⁵ Carbon tetrachloride (CT) can be biodegraded by denitrifying, iron-reducing, sulfate-reducing, acetogenic, and methanogenic bacteria. Depending on the bacteria and the environmental conditions, CT can be completely mineralized to carbon dioxide and chloride ions, but more commonly chloroform if formed as a daughter product. Chloroform tends to persist under denitrifying conditions, but can be degraded under sulfate-reducing and methanogenic conditions. It can also be oxidized by methanotrophic

⁴⁵ Boulding, R. 2001. Literature Reference File on Fate and Transport of Carbon Tetrachloride. Prepared for Argonne National Laboratory Environmental Research Division, 56+ pp.

Table 3.11 Biodegradable Resource Conservation and Recovery Act (RCRA)-Regulated Compounds

Substrate Compounds	Respiration		Fermentation	Oxidation	Cooxidation
	Aerobic	Anaerobic			
Straight-chain alkanes	+	+	+	+	+
Branched alkanes	+	+	+	+	+
Saturated alkyl halides		+		+	+
Unsaturated alkyl halides		+		+	
Esters, glycols, epoxides	+	+	+	+	
Alcohols	+	+		+	
Aldehydes, ketones	+	+		+	
Carboxylic acids	+	+		+	
Amides	+	+			
Esters	+	+			
Nitriles	+	+			
Amines	+	+			
Phthalate esters	+	+		+	
Nitrosamines		+			
Thiols					
Cyclic alkanes	+		+	+	+
Unhalogenated aromatics	+	+		+	
Halogenated aromatics	+	+		+	+
Simple aromatic nitro compounds	+	+			
Aromatic nitro compounds with other functional groups	+	+			+
Phenols	+	+	+	+	+
Halogenated side-chain aromatics	+		+	+	
Fused-ring hydroxy compounds	+				
Nitrophenols		+			
Halophenols	+			+	
Phenols-dihydrides polyhydrides	+			+	+
2- and 3-ring fused polycyclic hydrocarbons	+			+	
Biphenyls	+				
Chlorinated biphenyls	+				
4-ring fused polycyclic hydrocarbons	+				
5-ring fused polycyclic hydrocarbons	+				
Fused polycyclic hydrocarbons	+				
Organophosphates	+	+			
Pesticides and herbicides	+	+			

Source: U.S. EPA (1985).

bacteria in the presence of methane. Dichloromethane (DCM) typically forms as a degradation product of chloroform. DCM tends to resist degradation in reducing conditions, but it is readily degraded under aerobic conditions, as is chloroethane, another daughter product. In fact, there are bacteria that are capable of using DCM and chloroethane as sole substrates. This is unusual, because most microorganisms that can degrade toxic organic chemicals require an additional carbon source to provide the main energy for growth.

An understanding of degradation pathways (biotic and abiotic) is fundamental to the selection, design, and operation of soil and ground water remediation systems as covered in Part III of this book.

3.6 GUIDE TO MAJOR REFERENCES

Table 3.12 provides an index to major references in the following broad categories: (1) environmental chemistry, (2) soil and geochemistry, (3) aqueous geochemistry, and (4) biogeochemistry and subsurface microbial ecology. Sparks (1998) and Tan (1998) provide a good general introduction

to soil chemistry. The geochemistry texts identified in [Table 3.12](#) tend to focus more on the chemistry of rock-forming materials, which is useful for classification of geologic materials, but need to be used in combination with texts of soil mineralogy and weathering for developing geochemical interpretations of contaminated sites.

Stumm and Morgan (1995) is probably the most widely cited text on aqueous geochemistry. Other good recent texts include Drever (1997) and Chappelle (2001). Paul and Clark (1989) is a good source for more detailed information on soil microbiology and biochemistry. Section 4.8 discusses major references dealing with contaminant hydrogeology and microbiology of contaminated ground water.

Table 3.12 Index to Major References on Soil and Ground Water Geochemistry and Microbiology^a

Topic	References
Environmental Chemistry	
	Bonati (1993), Connel (1997), Fortescue (1980), Hutzinger (various dates), Irgolic and Martell (1985), Manahan (1999, 2000), Neilson (1999), Thornton (1983), Weiner (2000); <u>Biogeochemistry</u> : Hallberg (1981), Ingerson (1973), Schlesinger (1991), Zajic (1969)
Soil and Geochemistry	
General	<u>Soil Chemistry</u> : Bear (1964), Bohn et al. (1985), Bollag and Stotzky (1990–2000 — soil biochemistry), Bolt (1982), Bolt and Burggenwert (1978), Bonneau and Souchier (1982), Cresser et al. (1993), Fairbridge and Finkl (1979), Greenland and Hayes (1978, 1980), Marshall (1964, 1977), Sparks (1989, 1998), Sposito (1989), Tan (1998, 2000); <u>Geochemistry</u> : Berner (1981), Brookins (1988), Fortescue (1980), Goldschmidt (1954), Hawkes and Webb (1962), Mason (1966), Rankama and Sahama (1950), Richardson and McSween (1989), Wedephol (1974); <u>Geochemical Thermodynamics</u> : Anderson and Crerar (1993), Nordstrom and Munoz (1985)
Soil Fertility and Nutrient Chemistry	Barber (1984), Bayer (1968), Donahue et al. (1977), Dowdy et al. (1981), Plaster (1985), Soon (1985), Thompson and Troeh (1978), Tisdale and Nelson (1975), Troeh and Thompson (1993)
Mineralogy/Weathering	<u>Soil Mineralogy</u> : Dinauer (1977), Dixon and Weed (1989), Marshall (1964, 1977); <u>Clay Mineralogy</u> : Eslinger and Pevear (1988), Grim (1968), Theng (1974, 1979); <u>Rock Mineralogy</u> : Deer et al. (1977), Garrels and Christ (1965), Gribble and Hall (1992), Iler (1979 — silica), Mason and Berry (1968), Pirrson and Knopf (1958), Reeves and Brosler (1978), Silverman and Ehrlich (1964), Van Johnso and Maxwell (1981); <u>Trace Elements</u> : See Table 4.5; <u>Weathering</u> : Colman and Dethier (1986), Kittrick (1986)
Soil Organic Matter/Humic Substances	Aiken et al. (1985), Allard et al. (1991), Baker (1991a, 1991b, 1991c), Bayer (1968), Beck et al. (1994), Broadbent (1953), Christman and Gjessing (1983), Kononova (1966), Kubát (1992), MacCarthy et al. (1990), Magdoff et al. (1996), Manaskaya and Drozdova (1968), Schnitzer and Khan (1972, 1978), Stevenson (1982), Tate (1987)
Sorption/Ion Exchange/Complexation	<u>Chelation</u> : Barton and Hemming (1993); <u>Colloids</u> : Hiemenz (1986), Iler (1955), Van Olphen (1963, 1977); <u>Complexation</u> : Dzombak and Morel (1990), Theng (1979); <u>Ion Exchange</u> : Helfferich (1962), Marrinsky (1966); <u>Sorption</u> : Anderson and Rubin (1981); <u>Surface Chemistry</u> : Davis and Hayes (1986), Hiemenz (1986), Jaycock and Parfitt (1981), Sposito (1984), Sparks and Grundl (1999), Theng (1974), Yu (1997)
Aqueous Geochemistry	
Hydro(geo)chemistry	Chappelle (2001), Deutsch (1997), Drever (1997), Eriksson (1985), Faust and Aly (1981), Hem (1985), Lloyd and Heathcote (1985), Mazor (1990), Morel (1983), Pagendorf (1978), Pankow (1991), Stumm and Morgan (1995); <u>Symposia/Edited Volumes</u> : Back and Letaile (1981), Eriksson (1984), Faust and Hunter (1967), Ingerson (1973), Rice (1989), Stumm (1987); <u>Oil Field Waters</u> : Collins (1975)
Chemical Equilibria	Brookins (1988), Denbigh (1981), Garrels and Christ (1965), Harned and Owen (1958), Martell and Smith (1974–1982), Pytkowicz (1983), Sillen and Martell (1964), Smith and Missen (1982), Van Zeggeren and Storey (1970); <u>Electrochemistry</u> : Bard et al. (1985), Bockris and Reddy (1973), Davies (1967), Harned and Owen (1958), Robinson and Stokes (1965); <u>Soil Chemical Equilibria/Solution Chemistry</u> : Elprince (1986), Lindsay (1979), Sposito (1994); <u>Symposia/Edited Volumes</u> : Bernard (1986), Hem (1971), Jenne (1979), Melchior and Bassett (1990), Stumm (1967)
Other Topics	<u>Humic Substances</u> : Aiken et al. (1985), Baker (1991a, 1991b, 1991c), Beck et al. (1994), Christman and Gjessing (1983); <u>Hydrolysis</u> : Baes and Mesmer (1976); <u>Oxidation Potentials</u> : Brookins (1988), Latimer (1952)

Table 3.12 Index to Major References on Soil and Ground Water Geochemistry and Microbiology^a (Continued)

Topic	References
	Subsurface Microbial Ecology
General Microbiology and Microbial Ecology	Atlas (1988), Atlas and Bartha (1987), Gaudy and Gaudy (1980), Moat (1988), Pointdexter and Leadbetter (1986), Porter (1946), Rosswall (1973), Zehnder (1988); <u>Environmental/Contaminant Microbiology</u> : Mitchell (1991), see also Biogeochemistry above and Table 4.5
Subsurface Microbiology, Biology, and Ecology	<u>Soil</u> : Alexander (1971, 1977), Barton and Hemming (1993), Crossley et al. (1991), Edwards et al. (1988), Hattori (1973), Killham (1994), Lavelle and Spain (2001), Metting (1992, 1993), Parr et al. (1981), Paul and Clark (1989), Van Elsas et al. (1997); <u>Ground Water</u> : Chappelle (2001); <u>Papers</u> : Ghiorse and Wilson (1988), Harvey and Widdowson (1993)
Microbiology of Natural Geologic Systems	Ehrlich (1981), Kuznetsov (1962), Kuznetsov et al. (1963), Odum and Singleton (1993), Silverman and Ehrlich (1964), Zajic (1969); <u>Petroleum Microbiology</u> : Atlas (1984), Davis (1967), Litchfield and Clark (1973)

^a See Table 4.5 for major references on contaminant chemical behavior.

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Sources and Behavior of Subsurface Contaminants

4.1 DEFINITIONS OF CONTAMINATION

The Safe Drinking Water Act (SDWA) of 1974 defines the term *contaminant* broadly to include “any physical, chemical, biological, or radiological substance or matter in water.” This definition draws no distinction between contamination from natural and anthropogenic sources, and it does not distinguish between acceptable and unacceptable levels of contamination. Definitions of contamination from several other sources give some useful additional perspectives on the meaning of the term:

- A *contaminated* freshwater aquifer has been impaired in quality — directly or indirectly by human activity — to such a degree that the U.S. Public Health Service would not recommend it for drinking water (Deutsch, 1963).¹
- Ground-water *contamination* is the degradation of the natural quality of ground water as a result of human activity (U.S. EPA, 1977/T4.4).
- *Contaminants* are all solutes introduced into the hydrologic environment as a result of human activity regardless of whether the concentrations reach levels that cause significant degradation of water quality; *pollution* results when contaminant concentrations reach levels that are considered to be objectionable (Freeze and Cherry, 1979/T2.4).
- Boundaries of *polluted* ground-water zones are the lines at which the concentrations of all pollutants have fallen below the maximum permissible concentration for potable water, or where all water properties have taken on the normal values of the environment concerned (Matthess, 1982/T4.5).
- A *substance* is any organic or inorganic chemical, microorganism, radionuclide, or other material, such as sediment. Whether a substance is a *contaminant* depends on its association with adverse impacts and on other site-specific factors such as hydrogeology (OTA, 1984/T4.4).

This handbook adopts the middle ground taken by U.S. EPA (1977/T4.4). Natural ground waters may be *unsuitable* for a specified use, but the term *contamination* is reserved for degradation of natural water quality as a result of human activity. Whether the degree of contamination results in *unacceptable* degradation of ground water lies in the realm of psychology, sociology, political science, and law. This determination may be site specific and a matter of personal preference (i.e., ground water at a particular location may meet drinking water standards but not be considered potable by an individual due to bad taste), or it may be defined by law and regulation at the county, state, or national level. Even regulatory definitions of acceptable concentrations of specific contaminants may differ from the county to the national level, with the differences generally being based on different judgments as to the degree of risk posed by a specific contaminant.

¹ Deutsch, M. 1963. Ground-Water Contamination and Legal Controls in Michigan. U.S. Geological Survey Water Supply Paper 1691.

A definition of ground-water contamination tied to human activity does not necessarily require that the contaminants themselves be of artificial origin, although this is usually the case (Section 4.2.3). Acid-mine drainage from coal mining and intrusion of salt water into freshwater aquifers by overpumping are examples of natural contaminants being released due to human activity (see discussion of Categories IV and VI in Section 4.2.3).

4.2 EXTENT AND SOURCES OF SUBSURFACE CONTAMINATION

Ground-water contamination is not a new problem. Probably the earliest scientific documentation of disease spread by ground-water contamination is the classic work of Dr. John Snow, who in 1854 linked 500 deaths from cholera in London's Soho District to a single well (Stamp, 1964).² The U.S. Public Health Service (Stiles et al., 1927)³ probably conducted the earliest systematic scientific study of ground-water contamination. This research examined the movement, velocity, and persistence of chemical and bacterial pollutants in ground water at Fort Casell, NC. Fiedler (1936)⁴ provides one of the earliest systematic descriptions of the general geologic and hydrologic controls governing the migration of contaminants in various types of aquifers.

Identification of ground-water contamination as a serious environmental problem in the U.S. is relatively recent. Zanoni (1971/T4.4), in a review of the scientific literature on ground-water pollution and sanitary landfills, identified only one citation on the topic prior to 1950 (Calvert, 1932)⁵ and eight citations in the 1950s. That number jumped to 47 in the 1960s. The U.S. Department of Health, Education, and Welfare sponsored the first symposium in the U.S. devoted to ground-water contamination in 1961 (U.S. Public Health Service, 1961).⁶ Deutsch (1963 — footnote 1), in the first systematic state-level study, identified over 50 cases of actual or suspected ground-water contamination in Michigan. Lindorff and Cartwright (1977/T4.4), in a compilation of 116 case histories of ground-water contamination, listed twice as many references for the period 1970–1975 than for the entire period prior to 1970.

The 1980s has seen an explosion in the amount of scientific literature on ground-water contamination. The number of symposia on the topic seems to grow each year. Table 5.12 identifies more than 90 symposia and conference series that focus on or address issues of soil and ground-water contamination. Perhaps 1986 can be pinpointed as the year when the study of ground-water contamination became a discipline in its own right, with the publication of the first issue of the *Journal of Contaminant Hydrology*.

4.2.1 Extent of Contamination

A variety of factors make precise estimates of the extent of ground-water contamination in the U.S. difficult. These include (1) the great variety and ranges of toxicity of waste materials; (2) variable patterns of waste disposal and accidental release of contaminants in the ground; (3) variable patterns of ground-water use from wells; (4) differing behaviors of each contaminant in the soil, water, and rock environment; (5) the wide range in geologic and hydrologic conditions in different parts of the country; and (6) changes in hydrologic conditions in time (LeGrand, 1965).⁷

² Stamp, D.L. 1964. *The Geography of Life and Death*. Cornell University Press, Ithaca, NY, 160 pp.

³ Stiles, C.W., H.R. Crohurst, and G.E. Thompson. 1927. *Experimental Bacterial and Chemical Pollution of Wells via Ground Water, and the Factors Involved*. U.S. Public Health Service Hygienic Laboratory Bulletin 147.

⁴ Fiedler, A.G. 1936. *Occurrence of Ground Water with Reference to Contamination*. J. Am. Water Works Assoc. 28(12):1954–1962.

⁵ Calvert, C.K. 1932. Contamination of Ground Water by Impounded Garbage Waste. *Journal of the American Water Works Association* 24:266–270.

⁶ U.S. Public Health Service. 1961. *Proceedings of the 1961 Symposium, Ground Water Contamination*. U.S. Public Health Service Technical Report W61-5.

⁷ LeGrand, H.E. 1965. Patterns of Contaminated Zones of Water in the Ground. *Water Resources Research* 1(1):83–95.

In addition, many potentially hazardous contaminants are colorless, odorless, and tasteless, and therefore difficult to detect by passive means. Many of the synthetic organic chemicals require sophisticated and expensive sampling and analytical techniques, further burdening detection efforts. For example, one round of organic compound testing of the 3400 public water supply wells in Illinois required an estimated 4 to 5 years to complete (Illinois EPA, 1986).⁸ Systematic testing of the estimated 500,000 private wells in the state would not only be prohibitive in terms of cost, but extremely time-consuming.

An assessment of the extent and severity of contamination is further complicated by the almost exponential growth of the synthetic organic chemistry industry in the U.S. since the early 1940s. At least 63,000 synthetic organic chemicals are in common industrial and commercial use in the U.S., and this number continues to grow by approximately 500 to 1000 new compounds every year (U.S. EPA, 1979).⁹ The human health effects of many of these chemicals, particularly over long periods of time at low exposure levels, are not known. It would take many years to properly test all these compounds and then prepare a complete contamination assessment.

Nevertheless, a relatively small percentage of all ground water is estimated to be contaminated. Lehr (1982),¹⁰ using simple assumptions of total ground water and the extent of ground-water contamination, estimated that 0.2% was contaminated. The Office of Technology Assessment (OTA) (1984/T4.4) cited a range of 1 to 2%, and concluded that the extent of contamination is likely to be greater because substances known to contaminate ground water are used throughout society, whereas efforts to detect contamination have focused primarily on public drinking water supplies and point sources, such as landfills and hazardous waste sites. Furthermore, even if only a small percentage of potentially available ground water is contaminated, this percentage may be significant because (1) contamination is often near heavily populated areas, and (2) reliance on ground water is increasing.

4.2.2 Major Types of Contaminants

Over 200 chemical substances have been found in ground water, many of which could have potentially adverse impacts on human health (OTA, 1984/T4.4). This number includes approximately 175 organic chemicals, over 50 inorganic chemicals (metals, nonmetals, and inorganic acids), and radionuclides. Many of these chemicals occur naturally in ground water, especially minerals that dissolve from geologic earth materials contacting the water. Most of these, however, have been introduced to the ground-water system by humans (Section 4.2.3).

Page (1981/T4.4) tested the concentration of 56 toxic substances (9 heavy metals and 47 organic compounds) in over 1000 ground-water samples and over 600 surface water samples selected to be representative of the entire state of New Jersey. Each substance tested was found in detectable concentrations in one or more samples. Five organic compounds were found in more than 50% of the ground-water samples (1,1,1-trichloroethane, 78%; chloroform and carbon tetrachloride, 64%; 1,1,2-tri-chloroethylene, 58%; and trans-dichloroethylene, 50%). An additional 20 organic compounds were detected in 10 to 50% of the samples. This study concluded that overall, ground water was as polluted as surface water in New Jersey.

The Ground Water Supply Survey (GWSS) conducted by the U.S. EPA provided information on the frequency with which volatile organic compounds (VOCs) were detected in 466 randomly selected public ground-water supply systems (Westrick et al., 1984/T4.4). The survey detected one or more VOCs in 16.8% of the small systems and 28.0% of large systems sampled. Two or more VOCs were found in 6.8 and 13.4% of the samples from small and large systems, respectively. The two VOCs found most often were trichloroethylene (TCE) and tetrachloroethylene (PCE).

⁸ Illinois Environmental Protection Agency. 1986. A Plan for Protecting Illinois Groundwater. Illinois Environmental Protection Agency, Springfield, IL. [Note: This plan has been replaced by the 1987 Illinois Groundwater Protection Act]

⁹ U.S. Environmental Protection Agency (EPA). 1979. Environmental Assessment: Short-Term Tests for Carcinogens, Mutagens and Other Genotoxic Agents. EPA/615/9-79/003 (NTIS PB300-611).

¹⁰ Lehr, J.H. 1982. How Much Ground Water Have We Really Polluted? Ground Water Monitoring Rev. 2(1):4.

A reliable determination of the extent and severity of ground-water degradation and associated health risks in the U.S. is probably not feasible because (1) tens of thousands of sites where a potential exists for contamination are not being monitored, and (2) comprehensive analyses of water quality at hundreds of thousands of wells would be required (Miller, 1985/T4.4).

4.2.3 Major Sources of Contamination

The U.S. OTA (1984/T4.4) has grouped 33 types of ground-water contamination sources into six major categories (Table 4.1) based on the general nature of the contaminating activity. Figure 4.1 depicts a number of these sources.

Category I includes sources that are intentionally designed to discharge substances. Subsurface percolation systems such as septic tanks and cesspools, injection wells, and land application of wastewater or sludges fall within this category. Such systems are designed primarily to use the natural capacity of the soil materials to degrade wastewaters. Septic tanks and cesspools have been estimated to discharge the largest volume of wastewater into the ground and are the most frequently reported sources of ground-water contamination (U.S. EPA, 1977). More than 23 million homes in the U.S. rely on onsite wastewater disposal systems, and the use of septic system cleaners that remove grease and kill roots may result in ground-water contamination by halogenated hydrocarbons and heavy metals, respectively (Noss, 1989).¹¹

Injection wells are another potential source of contamination. Injected wastewaters are often placed in unusable zones to be assimilated with poor-quality ground water of natural origin. Current regulations prohibit injection of wastes into an underground source of drinking water (USDW) or contamination of a USDW by deep-well injection. Injection of hazardous wastes is regulated under EPA's Underground Injection Control Program. Injection of wastes can contaminate ground water in five major ways (U.S. EPA, 1985/T4.4):

1. Upward migration around the injection well casing through faulty construction
2. Upward migration through improperly plugged or completed wells placed in the injection zone from oil exploration or other reasons
3. Upward migration through faults or fractures in the confining layer
4. Lateral migration of injected wastes
5. Direct injection into a USDW (no longer permitted)

Land application, a popular and inexpensive method of disposing of wastewater and sludge, can pollute ground water in several ways: (1) organic and inorganic contaminants in directly applied wastewater can move directly into ground water if the soil's filtration capacity is exceeded, and (2) precipitation infiltrating through land-applied sludges may leach contaminants into the ground-water system. EPA (1983/T4.4) estimated that 40 to 50% of the municipal sludge generated every year is applied to the land.

Category II includes sources designed to store, treat, or dispose of substances, but not to release contaminants to the subsurface. Landfills, open dumps, local residential disposal, surface impoundments, waste tailings and piles, materials stockpiles, graveyards, aboveground and underground storage tanks, containers, open burning sites, and radioactive disposal sites all fall into this broad category. It is important to note here that while a number of sources in this category are considered "waste" sources (e.g., landfills, dumps, impoundments, etc.), many others are "nonwaste" sources, such as petroleum and other chemical products. Storage tanks, stockpiles, and a variety of containers with residues of commercial products have been found to contribute contaminants to ground water if not properly designed and maintained.

¹¹ Noss, R.R. 1989. Septic System Cleaners: A Significant Threat to Groundwater Quality. *Journal of Environmental Health* 51(4):201–204.

Table 4.1 Sources of Ground Water Contamination

Category I: Sources Designed to Discharge Substances

Subsurface percolation (e.g., septic tanks and cesspools)
Injection wells
 Hazardous waste
 Nonhazardous waste (e.g., brine disposal and drainage)
Nonwaste (e.g., enhanced recovery, artificial recharge, solution mining, and *in situ* mining)
Land application
 Wastewater (e.g., spray irrigation)
 Wastewater by-products (e.g., sludge)
 Hazardous waste
 Nonhazardous waste

Category II: Sources Designed to Store, Treat, or Dispose of Substances; Discharge through Unplanned Release

Landfills
 Industrial hazardous waste
 Industrial nonhazardous waste
 Municipal sanitary
Open dumps, including illegal dumping (waste)
Residential (or local) disposal (waste)
Surface impoundments
 Hazardous waste
 Nonhazardous waste
Waste tailings
Waste piles
 Hazardous waste
 Nonhazardous waste
Materials stockpiles (nonwaste)
Graveyards
Animal burial
Aboveground storage tanks
 Hazardous waste
 Nonhazardous waste
 Nonwaste
Underground storage tanks
 Hazardous waste
 Nonhazardous waste
 Nonwaste
Containers
 Hazardous waste
 Nonhazardous waste
 Nonwaste
Open burning and detonation sites
Radioactive disposal sites

Category III: Sources Designed to Retain Substances during Transport or Transmission

Pipelines
 Hazardous waste
 Nonhazardous waste
 Nonwaste
Materials transport and transfer operations
 Hazardous waste
 Nonhazardous waste
 Nonwaste

Table 4.1 Sources of Ground Water Contamination (*Continued*)

Category IV: Sources Discharging Substances as a Consequence of Other Planned Activities
Irrigation practices (e.g., return flow)
Pesticide applications
Fertilizer applications
Animal feeding operations
Deicing salts applications
Urban runoff
Percolation of atmospheric pollutants
Mining and mine drainage
Surface mine related
Underground mine related
Category V: Sources Providing Conduit or Inducing Discharge through Altered Flow Patterns
Production wells
Oil (and gas) wells
Geothermal and heat recovery wells
Water supply wells
Other wells (nonwaste)
Monitoring wells
Exploration wells
Construction excavation
Category VI: Naturally Occurring Sources Whose Discharge Is Created or Exacerbated by Human Activity
Ground water–surface water interactions
Natural leaching
Saltwater intrusion/brackish water upconing (or intrusion and other poor-quality natural water)

Source: OTA (1984).

Category III consists of sources designed to retain substances during transport or transmission. Such sources consist primarily of pipelines and materials transport or transfer operations. Contaminant releases generally occur by accident or neglect, for example, as a result of pipeline breakage or a traffic accident. Again, most substances subject to release from sources within this category are not wastes but raw materials or products to be used for some beneficial purpose.

Category IV includes those sources discharging substances as a consequence of other planned activities. This category contains a number of agriculturally related sources such as irrigation return flows, feedlot operations, and pesticide and fertilizer applications. A number of sources related to urban activities, such as highway desalting, urban runoff, and atmospheric deposition, are included. Surface and underground mine-related drainage also fall within this category. Sources in this category tend to be spread over large areas and are generally more difficult to regulate.

Category V comprises sources providing conduits or inducing discharge through altered flow patterns. Such sources include water, oil, and gas production wells, monitoring wells, exploration holes, and construction excavations. Ground-water contamination from production wells stems from poor installation and operation methods, and incorrect plugging or abandonment procedures. Such practices create opportunities for cross-contamination by vertical migration of contaminants.

Finally, Category VI includes naturally occurring sources whose discharge is induced or intensified by human activity. Ground water–surface water interactions, described in the previous section, and saltwater intrusion or upconing (ground-water movement upward as a result of pumpage) provide the basis for this category. Withdrawals that are significantly more than recharge can affect

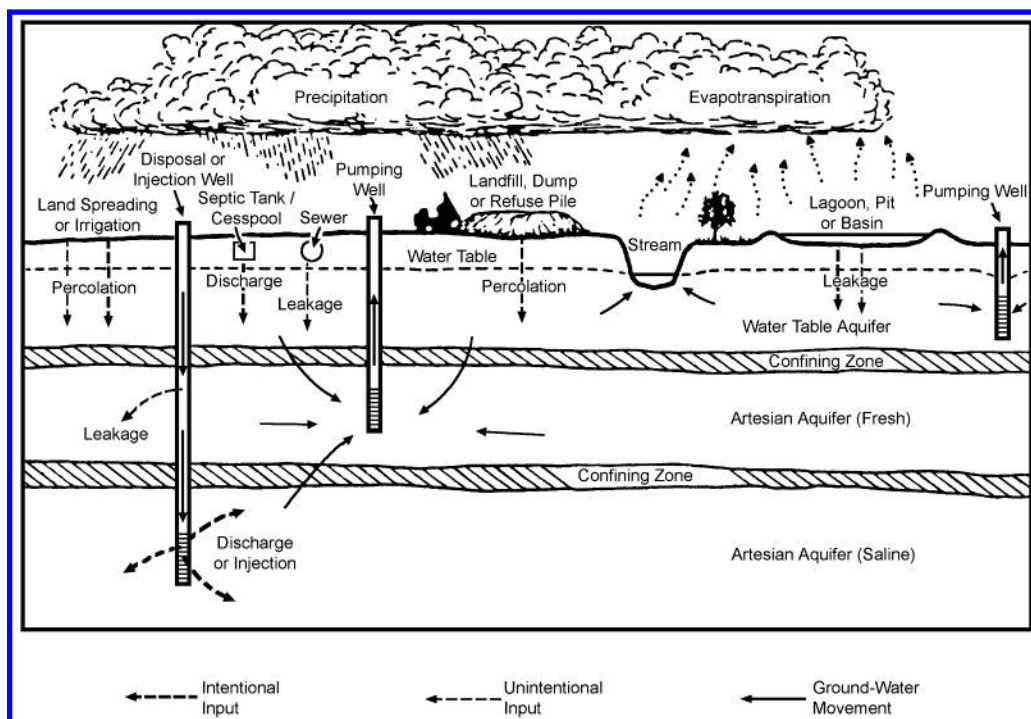


Figure 4.1 Sources of ground-water contamination (U.S. EPA, 1987a, after Geraghty and Miller, 1985).

ground-water quality. Saltwater intrusion in coastal areas and brine-water upconing from deeper formations in inland areas both can occur when pumpage exceeds an aquifer's natural recharge rate.

Contaminant releases are also referred to as originating from point or nonpoint sources. *Point sources* are those that release contaminants from a discrete geographic location, including leaking underground storage tanks, and ruptured or corroded transfer pipes (the cause of most fuel leaks), septic systems, and injection wells. *Non-point* sources of contamination are more extensive in area and diffuse in nature. It is therefore difficult to trace contaminants from non-point sources back to their origin. Agricultural activities (i.e., application of pesticides and fertilizers), urban runoff, and atmospheric deposition are potential nonpoint contaminant sources.

Systematic data on specific contaminants in ground water are not readily available for reasons discussed in [Section 4.2.1](#). [Table 4.2](#) shows types and sources of soil contamination from 100 sites in the Netherlands. Gasworks were the largest source of contamination (45%), followed by waste dumps and landfills (26%). The main contaminants identified at these sites were aromatic and halogenated hydrocarbons.

Palmer et al. (1988/T4.4) reviewed data on Superfund sites according to the primary hazardous substances detected ([Figure 4.2](#)). Sites contaminated by organics made up the largest group, including 136 sites; 78 sites were contaminated by heavy metals. Individual organic compounds frequently singled out as major contaminants include TCE, polychlorinated biphenyls (PCBs), toluene, and phenol. Arsenic and chromium are the most frequently identified individual heavy metal contaminants.

4.3 GENERAL MECHANISMS OF GROUND WATER CONTAMINATION

Contaminant releases to ground water can occur by design, by accident, or through neglect. Most ground-water contamination incidents involve substances released at or only slightly below

Table 4.2 Classification of Types and Sources of Soil Contamination in the Netherlands Based on a Sample of 100 Cases

Source of Contamination	Type of Contamination	Frequency (%)
Gasworks	Aromatic hydrocarbons, phenols, CN ⁻	45
Waste dumps and landfills	Halogenated hydrocarbons, alkyl-benzenes; metals like As, Pb, Cd, Ni, CN ⁻ ; pesticides	26
Chemicals production and handling sites (including painting industries and tanneries)	Halogenated hydrocarbons, alkyl-benzenes; metals like Pb, Cr, Zn, As	13
Metal plating and cleaning industries	Tri- and tetrachloroethylene, benzene, toluene, Cr, Cd, Zn, CN ⁻	9
Pesticide manufacturing sites	Pesticides, Hg, As, Cu	4
Automobile service facilities (including gasoline storage tanks)	Hydrocarbons, Pb	3

Source: Zoeteman (1985). © John Wiley & Sons. Reprinted by permission.

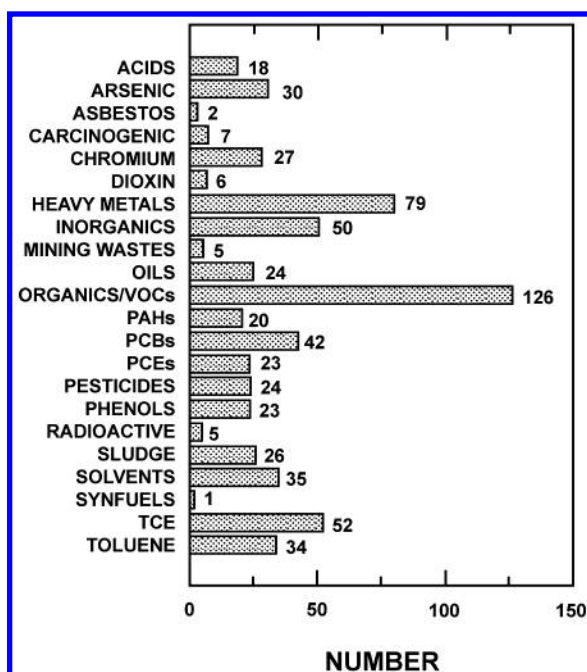


Figure 4.2 Major contaminants at Superfund sites (Palmer and Fish, 1991).

the land surface. Consequently, most contaminant releases affect shallow ground water initially. Certain activities, however, such as oil and gas exploration, deep-well waste injection, and pumping of ground water underlain by salt water, initially tend to affect deeper ground water.

Ground water contamination can occur by infiltration, recharge from surface water, direct migration, and interaquifer exchange. The first and second mechanisms primarily affect surface aquifers; the third and fourth may affect either surface or deep aquifers.

4.3.1 Infiltration

Infiltration is probably the most common ground-water contamination mechanism. A portion of the water that falls to the earth as precipitation slowly infiltrates the soil through pore spaces in the soil matrix. As the water moves downward under the influence of gravity, it dissolves materials with which it comes into contact. Water percolating downward through a contaminated

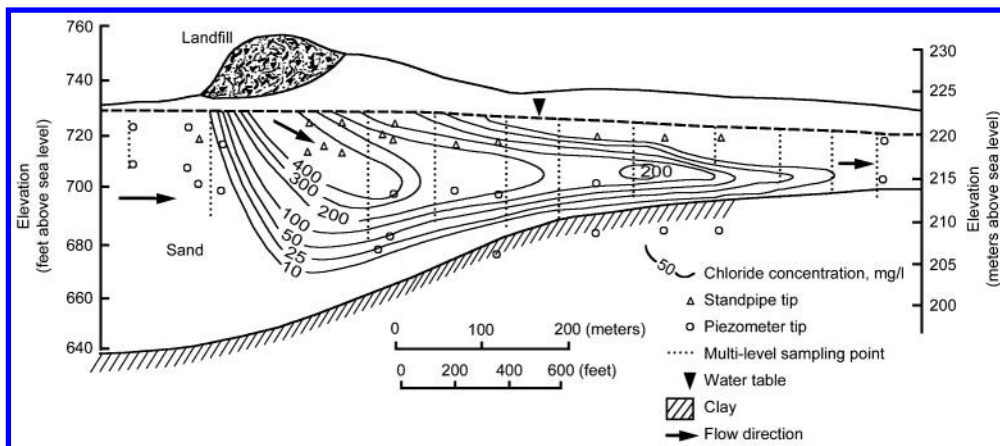


Figure 4.3 Plume of leachate migrating from a sanitary landfill on a sandy aquifer using contours of chloride concentration (U.S. EPA, 1987a, after Freeze and Cherry, 1979).

zone can dissolve contaminants, forming leachate that may contain inorganic and organic constituents. The leachate will continue to migrate downward under the influence of gravity until it reaches the saturated zone. In the saturated zone, contaminants in the leachate will spread horizontally in the direction of ground-water flow and vertically due to gravity (Figure 4.3). This process can occur beneath any surface or near-surface contaminant source exposed to the weather and the effects of infiltrating water. [Section 4.4.3](#) discusses how nonaqueous phase liquids (NAPLs) move into the subsurface.

4.3.2 Recharge from Surface Water

Normally, ground water moves toward or “discharges” to surface water bodies. However, movement of contaminants from surface water to ground water can occur in losing streams (where normal elevation of the water table lies below the stream channel) and during flooding. Flood stages may cause a temporary reversal in the hydraulic gradient, with a flow of contaminants into bank storage, or contaminant entry through improperly cased wells ([Figure 4.4a](#)). For example, Schwarzenbach et al. (1983)¹² documented movement of organic contaminants in river water into glacial sand and gravel aquifers in the Aare and Glatt valleys in Switzerland. Contaminated surface water can also enter an aquifer if the ground-water level adjacent to a surface water body is lowered by pumping ([Figure 4.4b](#)).

4.3.3 Direct Migration

Contaminants can migrate directly into ground water from below-ground sources (e.g., storage tanks, pipelines) that lie within the saturated zone. Much greater concentrations of contaminants may occur from these sources because of the continually saturated conditions. Storage sites and landfills excavated to a depth near the water table may also permit direct contact of contaminants with ground water. In addition, contaminants can enter the ground-water system from the surface by vertical leakage through the seals around well casings, through wells abandoned without proper procedures, or as a result of contaminant disposal through deteriorated or improperly constructed wells.

¹² Schwarzenbach, R., W. Giger, E. Hoehn, and J. Schneider. 1983. Behavior of Organic Compounds during Infiltration of River Water to Ground Water: Field Studies. *Environmental Science and Technology* 17(8):472–479.

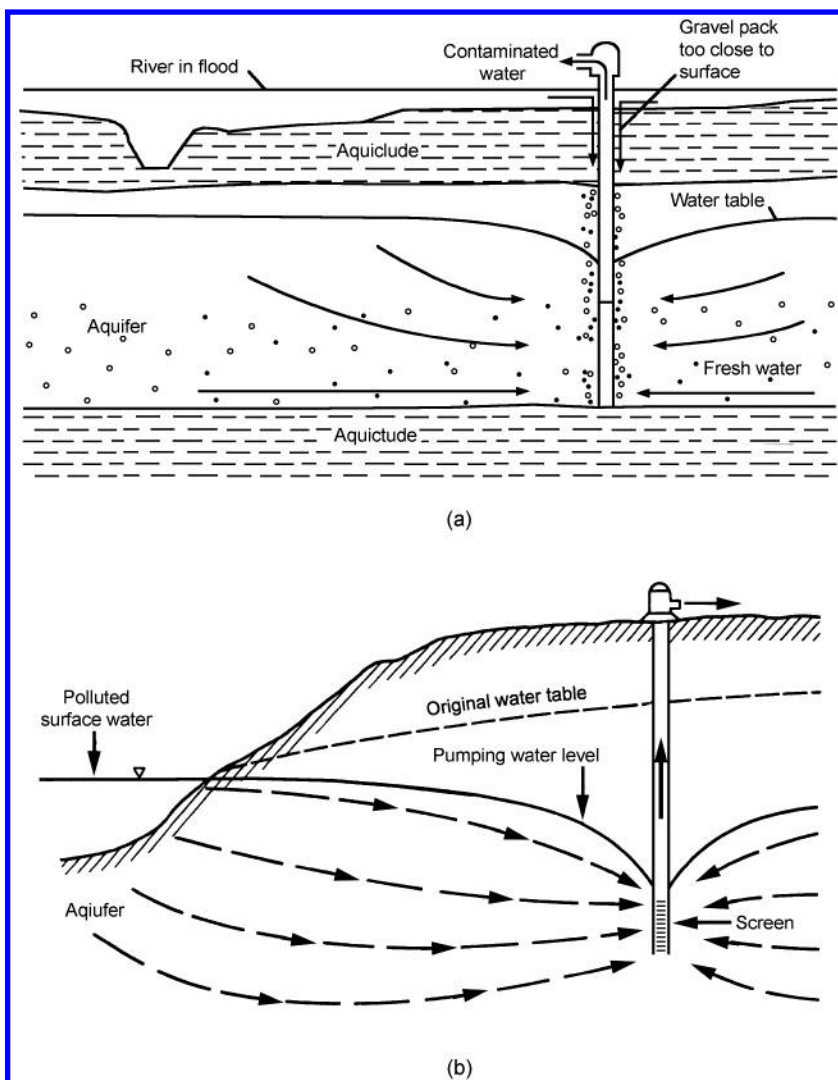


Figure 4.4 Ground-water contamination from surface water: (a) floodwater entering improperly cased well (Deutsch, 1963); (b) induced flow from pumping (Deutsch, 1965).

4.3.4 Interaquifer Exchange

Contaminated ground water can mix with uncontaminated ground water through a process known as interaquifer exchange, in which one water-bearing unit communicates hydraulically with another. This occurs most commonly in bedrock aquifers where a well penetrates more than one water-bearing formation to increase its yield. Each water-bearing unit has its own range of head potential. When the well is not being pumped, water moves from the formations with the greatest potential to formations of lesser potential. If the formation with the greater potential contains contaminated or poorer-quality water, it may degrade the quality of water in another formation.

In a process similar to that of direct migration, old and improperly abandoned wells with deteriorated casings or seals may contribute to interaquifer exchange. Vertical movement may be induced by pumping, or may occur under natural gradients. For example, [Figure 4.5](#) depicts an improperly abandoned well with a corroded casing that formerly tapped only a lower uncontaminated aquifer. The corroded casing allows water from an overlying contaminated zone to commu-

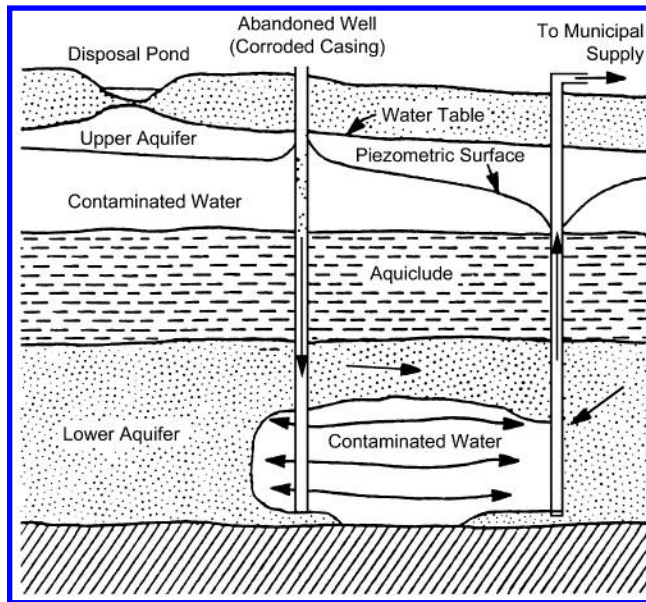


Figure 4.5 Vertical movement of contaminants along an old, abandoned, or improperly constructed well (U.S. EPA, 1977, after Deutsch, 1961).

nicate directly with the lower aquifer. The pumping of a nearby well tapping the lower aquifer creates a downward gradient between the two water-bearing zones. As pumping continues, contaminated water migrates through the lower aquifer to the pumping well. Downward migration of the contaminant may also occur through the confining layer that separates the upper and lower aquifers. However, the rate of contaminant movement through a confining layer is often much slower than the rate of movement through the direct connection of an abandoned well.

4.4 CONTAMINANT TRANSPORT PROCESSES

The extent to which a contaminant moves in ground water depends on its behavior in relation to various processes that encourage transport (Sections 4.4.1 through 4.4.5) and other processes that serve to retard movement (Section 4.5). The shape and speed of contaminant plumes are determined by these processes and by factors relating to the aquifer materials and characteristics of the contaminants (Section 4.7). In addition to the discussion in Chapter 3, EPA's Seminar Publication on Transport and Fate of Contaminants in the Subsurface (U.S. EPA, 1989/T4.5) and Part II (Physical and Chemical Processes in the Subsurface) of EPA's Seminar Publication on Site Characterization for Subsurface Remediation (U.S. EPA, 1991/T9.10) provide more detailed treatment of contaminant transport and retardation processes.

In broad terms, three processes govern the extent to which chemical constituents migrate in ground water: (1) advection, movement caused by the flow of ground water; (2) dispersion, movement caused by the irregular mixing of waters during advection; and (3) retardation, principally chemical mechanisms that occur during advection, which tend to slow down the rate of contaminant migration.

4.4.1 Advection

Ground water in its natural state is constantly in motion, although in most cases it is moving very slowly, typically at a rate of inches or feet per day. Ground-water flow, or advection, is

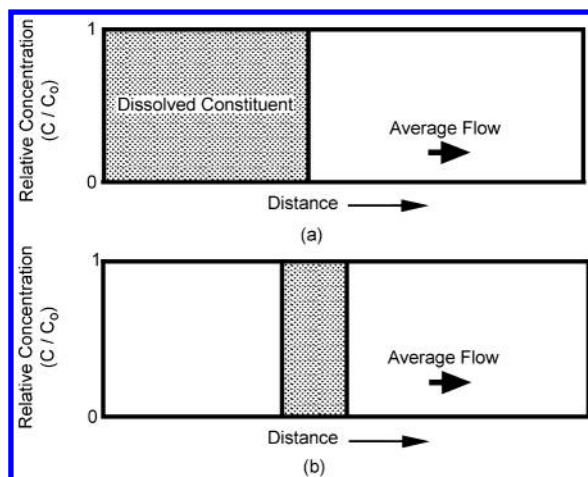


Figure 4.6 Movement of a concentration front by advection only: (a) continuous source; (b) slug (U.S. EPA, 1987a).

calculated using Darcy's law (Section 2.6.3) and is governed by the hydraulic principles discussed in Chapter 2. Time-of-travel calculations based on advective flow (Section 2.6.5) may *underestimate* the rate of migration of dissolved constituents such as chlorides and nitrates, which are minimally retarded by aquifer solids, as a result of hydrodynamic dispersion (Section 4.4.2). On the other hand, time-of-travel estimates may *overestimate* the rate of migration for contaminants subject to retardation processes.

Figure 4.6a shows the relative concentration of a dissolved constituent emanating from a constant source of contamination vs. distance along the flow path. Figure 4.6b shows a similar plot for a discontinuous contaminant source that produced a single slug of dissolved contaminant. Considering advective flow only, no diminution of concentration appears as a straight line moving at the rate of ground-water flow.

Several mechanisms influence the spread of a contaminant in the flow field. Dispersion and density/viscosity differences may accelerate contaminant movement, while various retardation processes slow the rate of movement compared to that predicted by simple advective transport.

4.4.2 Hydrodynamic Dispersion

Hydrodynamic dispersion is the net effect of a variety of microscopic, macroscopic, and regional conditions that influence the spread of a solute concentration front through an aquifer (Anderson, 1984; Schwartz, 1977).¹³ Quantifying dispersion may be important in fate assessment, because contaminants can move more rapidly through an aquifer by this process than by simple plug flow (i.e., uniform movement of water through an aquifer with a vertical front). In other words, physical conditions (such as the presence of permeable zones where water can move more quickly) and chemical processes (such as molecular diffusion of dissolved species to ground water with lower concentrations ahead of the contaminant front) result in more rapid contaminant movement than would be predicted by ground-water equations for physical flow, which assume average values for permeability.

Dispersion on the *microscopic* scale is caused by (1) external forces acting on the ground-water fluid, (2) variations in pore geometry, (3) molecular diffusion along concentration gradients, and (4) variations in fluid properties such as density and viscosity. Dispersion at this scale, also called

¹³ Anderson, M.P. 1984. Movement of Contaminants in Groundwater: Groundwater Transport: Advection and Dispersion. In: Groundwater Contamination, National Academy Press, Washington, D.C., pp. 37–45. Schwartz, F.W. 1977. Macroscopic Dispersion in Porous Media: The Controlling Factors: Water Resources Research 13(4):743–752.

mechanical dispersion, is generally less accurate than estimated advective flow and, for this reason, is often ignored. Lehr (1988)¹⁴ warns against putting forth too much effort to quantify dispersion at this scale.

Dispersion on the *macroscopic* scale is caused by variations in hydraulic conductivity and porosity, which create irregularities in velocity and consequent additional mixing of the solute. Over large distances, regional variations in hydrogeologic units can affect the amount of dispersion that occurs. Macroscopic dispersion may result in substantially faster travel times of contaminants than those predicted by equations for mechanical dispersion. Therefore, it should be the focus of efforts to characterize dispersion (Wheatcraft, 1989).¹⁵ Macroscopic features such as lenses of higher conductivity in unconsolidated materials, solution channeling, and fracturing are the major macroscopic features that may contribute to contaminant dispersion. Appendix C provides some empirical equations for estimating scale-dependent longitudinal and transverse horizontal and vertical dispersivities in sand, sand and gravel, gravel, and fractured rock aquifers.

Figure 4.7a shows the effect of dispersion as a plot of relative constituent concentration vs. distance along a flow path. In the figure, the front of the dissolved constituent distribution is no longer straight, but instead appears “smeared.” Some of the dissolved constituent actually moves ahead of what would have been predicted if only advection were considered. Figure 4.7b gives an aerial view of dispersion of a contaminant plume from a continuous source.

In a similar manner, the concentration of a slug of material introduced to a flow field appears as shown in Figure 4.8a, with the peak concentration declining over time and distance. In such a situation, the total mass of dissolved constituent remains the same; however, it occupies a larger volume, effectively reducing the concentration found at any distance along the flow path. An aerial view of intermittent sources affected by dispersion is shown in Figure 4.8b. Dispersion dilutes the concentration of a contaminant, thus reducing peak concentrations encountered in the groundwater system.

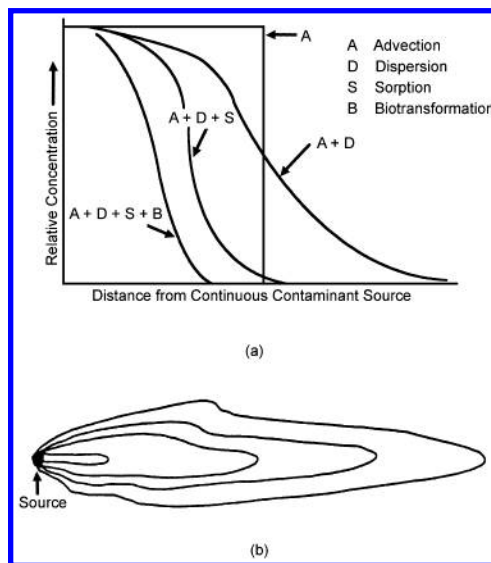


Figure 4.7 Effect of dispersion and retardation on movement of a contaminant front from a continuous source: (a) relative concentrations compared to advection only; (b) plan view of plume (U.S. EPA, 1987a).

¹⁴ Lehr, J.H. 1988. An Irreverent View of Contaminant Dispersion. Ground Water Monitoring Rev. 8(4):4–6.

¹⁵ Wheatcraft, S.W. 1989. An Alternate View of Contaminant Dispersion. Ground Water Monitoring Review 9(3):11–12.

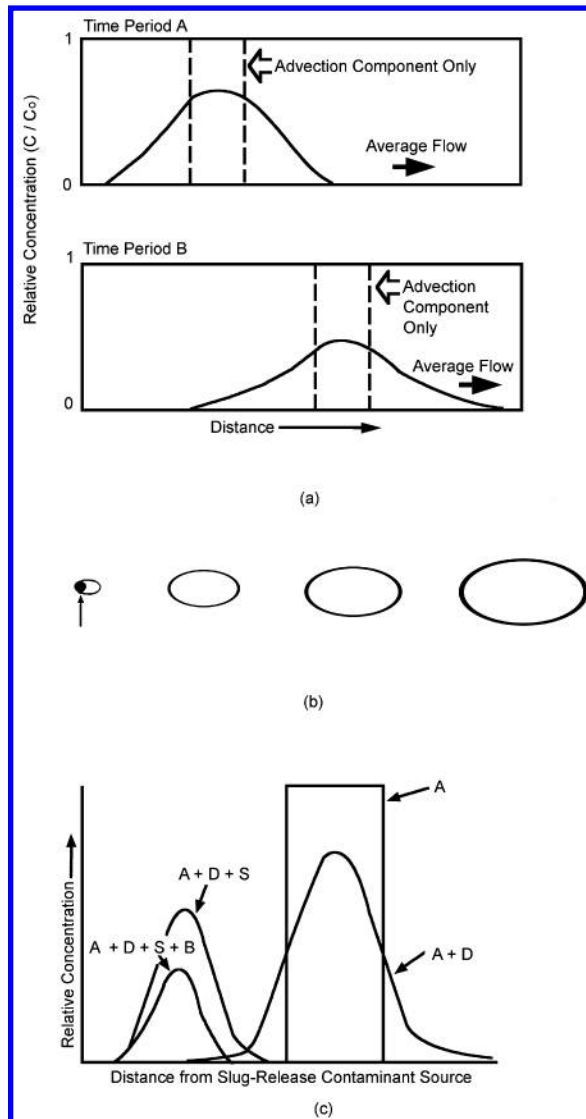


Figure 4.8 Effect of dispersion and retardation on movement of a contaminant slug; (a) dispersion over time; (b) plan view of plume from intermittent point source; (c) sorption and biodegradation (U.S. EPA, 1987a).

4.4.3 Density/Viscosity Differences

Contaminants having a density lower than that of ground water tend to concentrate in the upper portions of an aquifer, while those having a higher density concentrate in the lower portions. The viscosity (tendency to resist internal flow) of specific contaminants affects their rate of migration through soil and within an aquifer. Density and viscosity effects are significant when nonaqueous phase liquids are present in the subsurface, and where the salinities of ground waters contrast strongly (freshwater and saltwater).

Nonaqueous Phase Liquids. NAPLs moving through the subsurface can displace both water and air. Water in the presence of NAPLs tends to line the edges of the pores and adhere to soil particles, while the NAPL tends to move through the central portions of the pores. In unsaturated soil, when neither water nor the NAPL occupies the entire pore space, the NAPL and water move

more slowly through the soil than they would if one or the other filled the pore space. A certain percentage of nonaqueous phase liquids will adhere to soil particles in the vadose zone (called *residual saturation*), with further movement dependent on volatilization or dissolution by percolating ground water.

The behavior and movement of NAPLs that are lighter than water (LNAPL) differ from those that are denser than water (DNAPLs). Figure 4.9 illustrates the movement of a spill of an LNAPL in the subsurface. If the amount of product spilled is small, the LNAPL will flow into the unsaturated zone until residual saturation is reached (Figure 4.9a). Infiltrating water will gradually dissolve components of the LNAPL, such as benzene, toluene, and xylene, and carry the contaminants to the ground water. Since LNAPLs tend to be volatile, some of the spilled material will also partition into the soil air and move through the vadose zone by molecular diffusion. Parts of the gaseous phase may also be dissolved by percolating water and enter the ground water by that path. The movement of soil gas in the vadose zone does not necessary follow the ground-water

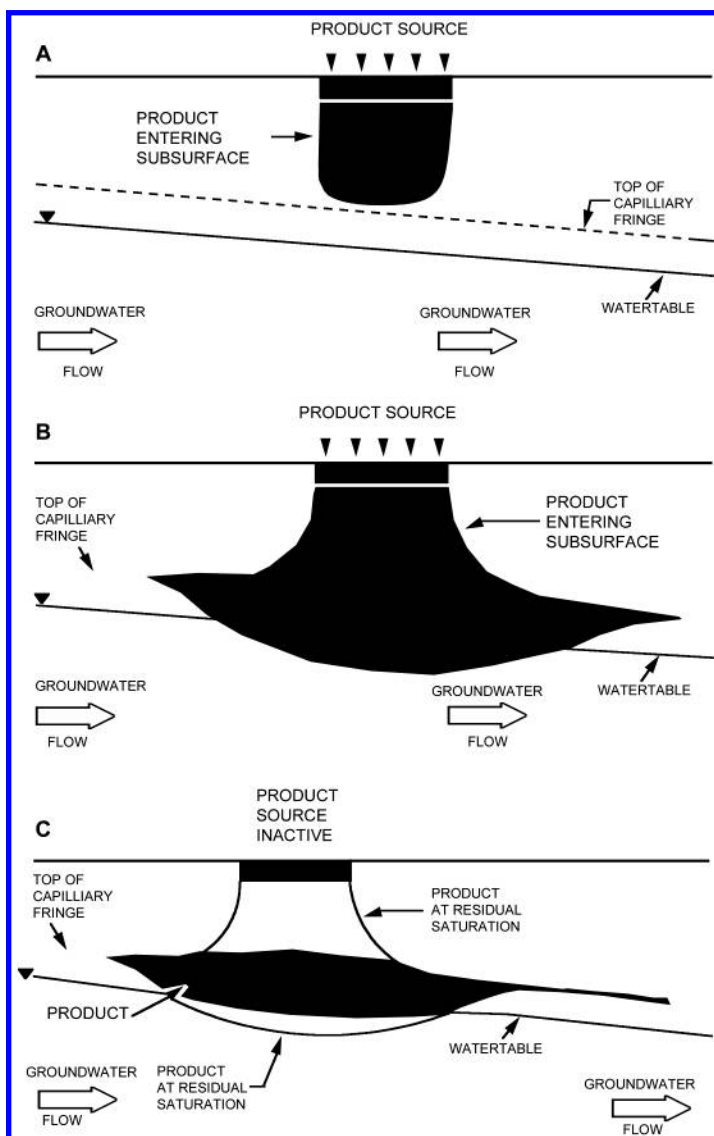


Figure 4.9 Movement of LNAPLs into the subsurface (Palmer and Johnson, 1989b).

gradient, so soil gas measurements must be supplemented to ground-water sampling to delineate contaminant plumes.

A larger spill will result in product reaching the water table. The dissolved components of the infiltrating NAPL precede the product and may change the wetting properties of the water, causing a reduction in the residual water content and a collapse of the capillary fringe and depression of the water table (Figure 4.9b). If the flow from the NAPL source is stopped, it will flow through the vadose zone until residual saturation is reached. The NAPL will then tend to spread laterally along the top of the capillary fringe (Figure 4.9c).¹⁶ Draining of the upper portions of the vadose zone reduces the total head at the interface between the NAPL and the ground water, allowing the water table to rebound somewhat. However, product remains in the aquifer at residual saturation and is gradually released by dissolution as ground water moves through this zone.

DNAPLs can be very mobile in the subsurface as a result of their relatively low solubility, high density, and low viscosity. Figure 4.10 illustrates the behavior of spilled DNAPLs in the subsurface. Displacement of water, which has a lower density and higher viscosity than DNAPLs, creates an unstable liquid front with viscous fingering resulting. A relatively small spill will result in fingers of DNAPL penetrating the vadose zone until residual saturation is reached. A contaminant plume in ground water generally develops as a result of dissolution by percolating water and dense vapors that come in contact with the capillary fringe (Figure 4.10a).

A larger spill may result in flow of the DNAPL until it reaches the capillary fringe. If the thickness is sufficient to overcome the capillary force between the water and the aquifer matrix, it will flow into the saturated zone and continue until residual saturation is reached (Figure 4.10b). A very large spill can result in penetration to the bottom of the aquifer, with pools of DNAPL forming in depressions. Figure 4.10c illustrates how a DNAPL can actually flow against the direction of ground-water flow when the impermeable base of an aquifer is sloping.

Ground Water Density Effects. Freshwater is less dense than water with high concentrations of dissolved solids. For example, in coastal areas, freshwater tends to float on top of seawater where sediments are hydrologically connected with the ocean. Pumping of ground water can disrupt this equilibrium, resulting in contamination of freshwater aquifers by sodium chloride. Consideration of density differences is essential when modeling interactions between freshwater and seawater (Frind, 1982).¹⁷ Density variations in ground water in deep boreholes may also result in errors in estimating flow directions, because they do not necessarily follow hydraulic gradients (Oberlander, 1989).¹⁸

Temperature Effects. The viscosity of water decreases as temperature increases. For example, Sniegocki (1963)¹⁹ found that viscosity differences resulting from surface water at 66°F injected into ground water at 43°F reduced the specific capacity (gallons per minute per foot of drawdown) of an artificial recharge well in the Grand Prairie Region in Arkansas by 30%. Kaufman and McKenzie (1975),²⁰ on the other hand, observed that the apparent hydraulic conductivity of an injection zone in the Floridan aquifer receiving hot organic wastes increased about 2.5 times because of temperature differences alone.

¹⁶ The term *free product*, although it is often used when describing subsurface flow of NAPLs at concentrations above residual saturation, is not strictly correct in this context. Where an LNAPL occupies most of the pore space, the LNAPL will seep from pore space into a borehole cavity and form free product that floats on the surface of the ground water, but free product in the matrix pure fuel will not fill 100% of the pore space. For example, at the capillary fringe there exists more of a mixing zone where hydrocarbon saturation gets up to a certain level, but does not displace water completely.

¹⁷ Frind, E.O. 1982. Simulation of Long-Term Transient Density-Dependent Transport in Groundwater. *Advances in Water Resources* 5(June):73–88.

¹⁸ Oberlander, P.L. 1989. Fluid Density and Gravitational Variations in Deep Boreholes and Their Effect on Fluid Potential. *Ground Water* 27(3):341–350.

¹⁹ Sniegocki, R.T. 1963. Problems in Artificial Recharge through Wells in the Grand Prairie Region, Arkansas. U.S. Geological Survey Water Supply Paper 1615-F.

²⁰ Kaufman, M.I and D.J. McKenzie. 1975. Upward Migration of Deep-Well Waste Injection Fluids in Floridan Aquifer, South Florida. *Journal of Research of the U.S. Geological Survey* 3:261–271.

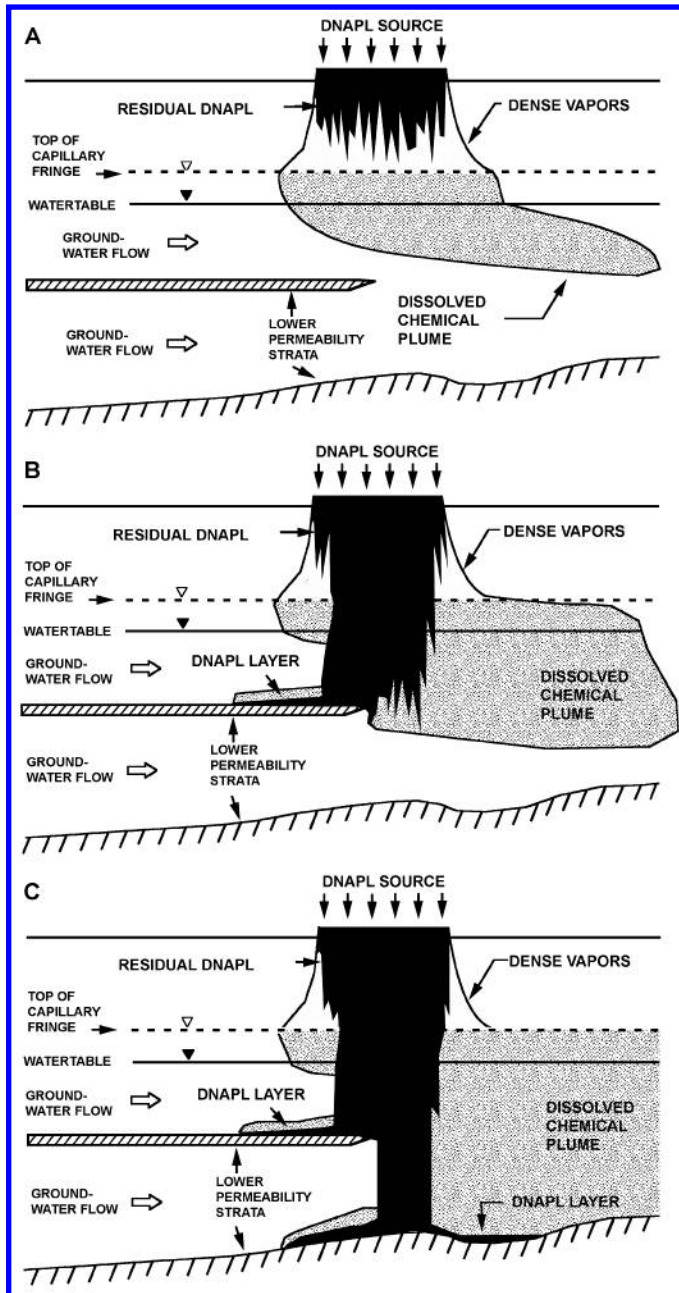


Figure 4.10 Movement of DNAPLs into the subsurface (Palmer and Johnson, 1989b).

4.4.4 Osmotic Potential

Osmotic potential, the energy required to pull water away from ions in solution that are attracted to polar water molecules, is a primary factor affecting solute transport in the vadose zone (see Section 2.4.1). Shales that serve as confining layers can sometimes act as semipermeable membranes, if the ionic concentrations on both sides of the clay layer differ greatly (Hanshaw, 1972).²¹ Bredehoeft et al. (1963)²² have suggested this as a mechanism for the development of brines in deep sedimentary basins where concentrations three to six or more times the concentration of seawater occur. In laboratory experiments, Kharaka (1973)²³ found that ion mobility across geologic membranes varied with the material, but that monovalent and divalent cations generally followed the same sequences: $\text{Li} < \text{Na} < \text{NH}_3 < \text{K} < \text{Rb} < \text{Cs}$ and $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba}$. Osmosis, if it occurs at all, is likely to occur in deep sedimentary basins rather than near-surface aquifers, where salinities are higher and strong contrasts in ionic strength between water-bearing units are more likely to exist.

4.4.5 Facilitated Transport

Facilitated transport, in which the mobility of a contaminant is increased relative to expected retardation by adsorption to subsurface solids, is a relatively new area of study in the field of contaminant transport. Processes such as chelation (the formation of complex ions with organic ligands) have long been known to increase the mobility of metal ions because the bonding sites that would be available to the substrate become occupied by the chelating agent. More recently, attention has been focused on increased mobility of organic compounds by (1) *cosolution* (increased solubility of hydrophobic organic contaminants when water-miscible organic solvents, such as ethanol, methanol, and acetone, are present in ground water), and (2) attachment to colloidal particles that are often mobile in the unsaturated and saturated zones of the subsurface (Huling, 1989/T4.5). In addition, when DNAPLs, such as chlorinated solvents, and LNAPLs are both present at a site, the DNAPL can dissolve the LNAPL and carry it beneath the water to deeper aquifer zones.

4.5 CONTAMINANT RETARDATION

In ground-water contaminant transport, a number of chemical and physical mechanisms retard or slow the movement of constituents in ground water. Four major mechanisms that retard contaminant movement are (1) filtration, (2) sorption, (3) precipitation, and (4) transformation or degradation.

Figure 4.7a and Figure 4.8c illustrate the movement of a concentration front by advection only (A), advection plus dispersion (A + D), and with the addition of sorption, a partitioning process (A + D + S). The greatest retardation, however, results from the combined effects of advection, dispersion, sorption, and biotransformation (A + D + S + B). The amount of retardation resulting from sorption, other partition processes, and biotransformation depends on physical and chemical properties of the aquifer, including biologic populations, and chemical properties of the contaminant.

²¹ Hanshaw, B.B. 1972. Natural-Membrane Phenomena and Subsurface Waste Emplacement. In: Symposium on Underground Waste Management and Environmental Implications, T.D. Cook (ed.), American Association of Petroleum Geologists Memoir 18, pp. 308–315.

²² Bredehoeft, J.D., C.R. Blyth, W.A. White, and G.B. Maxey. 1963. Possible Mechanism for Concentration of Brines in Subsurface Formations. Bulletin of the American Association Petroleum Geologists 47(2):257–269.

²³ Kharaka, Y.K. 1973. Retention of Dissolved Constituents of Waste by Geologic Membranes. In: Symposium on Underground Waste Management and Artificial Recharge, J. Braunstein (ed.), International Association of Hydrological Sciences Publication 110, pp. 420–435.

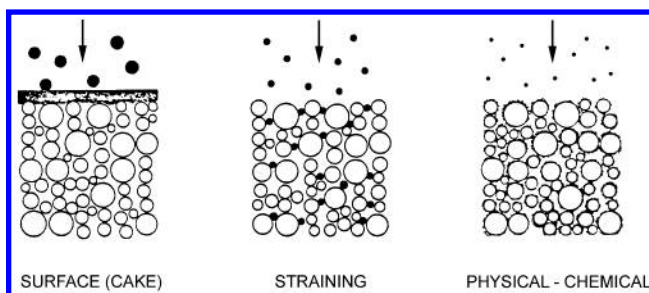


Figure 4.11 The three filtration mechanisms that limit particle migration through porous media (Palmer and Johnson, 1989a, after McDowell-Boyer et al., 1986).

4.5.1 Filtration

Filtration is the entrapment of solid particles and large dissolved molecules in the pore spaces of the soil and aquifer media. Figure 4.11 shows three major mechanisms of filtration: surface filtration, straining, and physical–chemical interactions. *Surface filtration* results when particles are larger than the pore spaces and form a cake on the surface, at which the pore size becomes too small. Caking may also result from biological activity, as in the clogging mat that develops in septic tank absorption trenches. *Straining* happens when the particles are about the same size as the pore spaces. In this process, particles move through pores until they become lodged at the entrance to a pore that is too small. Filtration resulting from *physical–chemical interactions* with solid surfaces is discussed under partitioning process in the next section.

Filtration limits flow by clogging pore spaces and reducing the hydraulic conductivity of the material. Most dissolved species are retarded by partitioning or transformation, but if the molecular size of a chemical reaction product exceeds the pore size of the soil or aquifer, mechanical filtration occurs. Flocculation of colloidal material resulting from the precipitation of iron and manganese oxides, as well as clogging resulting from microbial activity, may hinder the movement of dissolved constituents. Gas bubble formation may also eventually clog pore spaces, resulting in a filtering effect. For example, a 10% increase in the air content of media voids can cause a 15% decrease in effective porosity, resulting in a 35% decrease in permeability, and about a 50% reduction in dispersion (Orlob and Radhakrishna, 1958).²⁴

Filtration may also result in residual contamination that is highly resistant to both mobilization by desorption into air and water and microbial degradation. For example, the soil fumigant 1,2-dibromomethane, which is readily biodegraded under aerobic conditions, has been found in agricultural soils up to 19 years after its last known application, due to entrapment in soil micropores (Steinberg et al., 1987).²⁵

4.5.2 Sorption

Ion exchange involves the replacement of a cation attached to a negatively charged site on a mineral surface by another cation. The mineralogy and cation exchange capacity of an aquifer gives a general indication of its effectiveness in retarding cationic contaminants. As long as the ionic contaminant has a greater affinity for the solid surface than for existing adsorbed ions, retardation will occur. Once the exchangeable sites are filled, the contaminant will travel unretarded (see A + D + S curve in Figure 4.7a and Figure 4.8c). Precise predictions of retardation by ion exchange are not possible because of interactions among multiple ions. Furthermore, changes in environ-

²⁴ Orlob, G.T. and G.N. Radhakrishna. 1958. The Effects of Entrapped Gases on the Hydraulic Characteristics of Porous Media. Transactions of the American Geophysical Union 39(4):648–659.

²⁵ Steinberg, S.M., J.J. Pignatello, and B.L. Sawhney. 1987. Persistence of 1,2-Dibromomethane in Soils: Entrapment in Intraparticle Micropores. Environmental Science and Technology 21:1201–1213.

mental conditions such as pH and Eh (Section 4.7.2) or ground-water solution composition may remobilize contaminants formerly bound to geologic materials. In fact, the release of ions by exchange processes may aggravate a contamination problem. For example, Rovers et al. (1976)²⁶ observed release of aluminum to solution from soil contaminated by industrial waste.

Most organic contaminants are nonionic, and consequently, partitioning to aquifer solids usually occurs by *physical adsorption* processes such as Van der Waals and hydrophobic bonding (Section 3.2.2).

The *adsorption isotherm* is a measure of changes in the amount of a substance adsorbed at different concentrations at a constant temperature. It is the simplest and most widely used method for predicting physical adsorption. Empirical constants can be calculated from adsorption isotherms, and these constants then can be used to predict the amount of adsorption at concentrations other than those measured. However, this method assumes that temperature and other environmental conditions are the same as those under which the isotherms were measured originally.

There are three major types of adsorption isotherms: (1) the *linear distribution coefficient*, (2) the *Langmuir* adsorption isotherm, and 3) the *Freundlich* adsorption isotherm.

Linear Distribution Coefficient. The simplest type of isotherm is the linear distribution coefficient, K_d (also called the partition coefficient, K_p), which assumes that the amount of contaminant sorbed is directly proportional to the concentration of the compound in solution. The equation for calculating adsorption at different concentrations is

$$S = K_d C \quad (4.1)$$

where:

S = amount sorbed ($\mu\text{g/g}$ solid)

C = concentration of substance in solution ($\mu\text{/ml}$)

K_d = distribution coefficient

This equation is widely used to describe adsorption in soil and near-surface aquatic environments because many organic chemicals exhibit linear sorption behavior. Another widely used linear coefficient is the organic carbon partition coefficient (K_{oc}), which is equal to the distribution coefficient divided by the percentage of organic carbon present in the system ($K_{oc} = K_d / \% \text{ organic carbon}$), as proposed by Hamaker and Thompson (1972).²⁷ Equations are available for predicting the K_{oc} of both polar and nonpolar organic molecules based on molecular topology, provided the organic matter percentage exceeds 0.1% (Sabljic, 1987).²⁸ Karickhoff (1984)²⁹ discusses in some detail sorption processes of organic pollutants in relation to K_{oc} .

There are several major problems associated with using the linear distribution coefficient for describing adsorption–desorption reactions in ground-water systems (Reardon, 1981).³⁰ Some of these problems include:

- The coefficient actually measures multiple processes (reversible and irreversible adsorption, precipitation, and coprecipitation). Consequently, it is a purely empirical number with no theoretical basis on which to predict adsorption under differing environmental conditions, or to give information on the types of bonding mechanisms that are involved in the adsorption.

²⁶ Rovers, F.A., H. Mooij, and G.J. Farquhar. 1976. Contaminant Attenuation: Dispersed Soil Studies. In: Residual Management by Land Disposal, W.H. Fuller (ed.), EPA 600/9-76/015 (NTIS PB256 768), pp. 224–234.

²⁷ Hamaker, J.W. and J.M. Thompson. 1972. Adsorption. In: Organic Chemicals in the Soil Environment, Vol. I, C.A.I. Goring and J.W. Hamaker (eds.), Marcel Dekker, New York, pp. 49–143.

²⁸ Sabljic, A. 1987. On the Prediction of Soil Sorption Coefficients of Organic Pollutants from Molecular Structure: Application of Molecular Topology Model. Environmental Science and Technology 21(4):358–366.

²⁹ Karickhoff, S.W. 1984. Organic Pollutant Sorption in Aquatic Systems. Journal of Hydraulic Engineering 110:707–735.

³⁰ Reardon, E.J. 1981. K_d's: Can They Be Used to Describe Reversible Ion Sorption Reactions in Contaminant Migration? Ground Water 19(3):279–286.

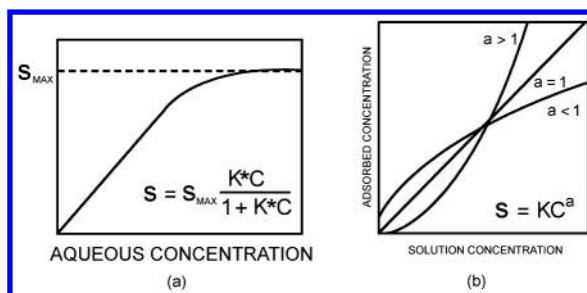


Figure 4.12 Adsorption isotherms: (a) Langmuir; (b) Freundlich (Palmer and Johnson, 1991).

- Contaminated aquifers may undergo a dynamic chemical evolution in which changing environmental parameters may result in variations of K_d values by several orders of magnitude at different locations and at the same location at different times.
- All methods used to measure the K_d value involve some disturbance of the solid material and, consequently, may not accurately reflect *in situ* conditions. Furthermore, K_d values taken from the literature may have been developed using solid material that differs significantly in physical and chemical characteristics from the site of interest.

In spite of these shortcomings, K_d values from the published literature can provide a qualitative assessment of a contaminant's mobility, and adsorption batch laboratory tests using simulated contaminated solutes and samples of actual soils or aquifer materials from a site can provide valuable information about contaminant behavior. Use of adsorption batch tests is required for more accurate assessment of contaminant fate and transport because they allow evaluation of sorption as a function of varying subsurface properties (organic carbon, grain size distribution, and mineralogy). This information, in turn, can be used to assign different values of K_d in numerical subsurface flow and transport models.

Langmuir Equation. The Langmuir adsorption equation was originally developed to describe adsorption of gases on homogeneous surfaces and is commonly expressed as follows:

$$C/S = 1/kS_{\max} + 1/CS_{\max} \quad (4.2)$$

where:

S_{\max} = maximum adsorption capacity ($\mu\text{g/g}$ soil)

k = Langmuir coefficient related to adsorption bonding energy ($\text{ml}/\mu\text{g}$)

S = amount adsorbed ($\mu\text{g/g}$ solid)

C = concentration of adsorbed substance in solution (μ/ml)

A plot of C/S vs. $1/C$ allows the coefficients k and S_{\max} to be calculated. When kC is much less than 1, adsorption will be linear as represented by Equation 4.1. Figure 4.12a shows the graphic form of the Langmuir isotherm and a different form of the basic equation.

The Langmuir model has been used to describe adsorption behavior of some organic compounds at near-surface conditions (Alben et al., 1988).³¹ However, the Langmuir model makes three important assumptions:

³¹ Alben, K.T., E. Shpirt, and J.H. Kaczmarczyk. 1988. Temperature Dependence of Trihalomethane Adsorption on Activated Carbon: Implications for Systems with Seasonal Variations in Temperature and Concentration. *Environmental Science and Technology* 22:406–412.

- The energy of adsorption is the same for all sites and is independent of degree of surface coverage.
- Adsorption occurs only on localized sites with no interaction between adjoining adsorbed molecules.
- The maximum adsorption capacity (S_{\max}) represents coverage on only a single layer of molecules.

These assumptions do not generally hold true in a complex heterogeneous media such as soil (Rao and Davidson, 1980).³² For example, Bailey et al. (1968),³³ in a study of adsorption of organic herbicides by montmorillonite, found that none of the compounds conformed to the Langmuir adsorption equation. Of the 23 compounds they tested, however, only a few did not conform well to the Freundlich equation, discussed below.

Freundlich Equation. The Freundlich equation is expressed as

$$S = KC^a \quad (4.3)$$

where:

S and C are as defined in Equation 4.2

K and a = empirical coefficients

Figure 4.12b shows the shape of the Freundlich isotherm at different values of a .

Taking the natural logarithms of both sides of Equation 4.3:

$$\ln S = \ln K + (a) \ln C \quad (4.4)$$

Thus, a log-log plot of S vs. C provides an easy way to obtain values for K (the intercept) and a (the slope of the line). When values for K and a have been obtained, the amount of sorption at a given concentration can be calculated using Equation 4.3. The log-log plot can also be used for graphic interpolation of adsorption at other concentrations. When $a = 1$, Equation 4.3 simplifies to Equation 4.1 (i.e., adsorption is linear).

4.5.3 Retardation by Sorption

When a migrating contaminant interacts with aquifer solids by sorption, movement is retarded relative to the movement of a noninteracting dissolved constituent in ground water. The *retardation factor* R_f is defined as the average velocity of the groundwater (v_w) divided by the average velocity of the retarded contaminant (v_c):

$$R_f = v_w/v_c \quad (4.5)$$

The retardation factor can be measured empirically by injecting a known amount of chemical compound along with a conservative (nonreactive) tracer and arrival time of the chemical of interest compared to that of the tracer. It can also be estimated if the linear distribution coefficient K_d is known (Section 4.5.2). The distribution coefficient K_d is related to the retardation factor R_f by the equation (Cohen and Mercer, 1993/T9.10)

$$R_f = [1 + (\rho_b/n)K_d] \quad (4.6)$$

³² Rao, P.S.C. and J.M. Davidson. 1980. Estimation of Pesticide Retention and Transformation Parameters Required in Nonpoint Source Pollution Models. In: Environmental Impact of Nonpoint Source Pollution, M.R. Overcash and J.M. Davidson (eds.), Ann Arbor Science Publishers, Ann Arbor, MI, pp. 23–67.

³³ Bailey, G.W., J.L. White, and T. Rothberg. 1968. Adsorption of Organic Herbicides by Montmorillonite: Role of pH and Chemical Character of Adsorbate. Soil Science Society of America Proceedings 32:222–234.

where:

n = porosity

ρ_b = bulk density of the porous media

This equation assumes that the aquifer is uniform and sorption is linear, reversible, and instantaneous.

Bulk mass density is related to particle mass density, ρ_s , by the following:

$$\rho_b = \rho_s (1 - n) \quad (4.7)$$

where:

$\rho_s = 2.65$ to 2.70 g/cm^3 for most mineral soils

Although many organic chemicals exhibit linear sorption behavior, they may not exhibit the same behavior for desorption. The assumption of fully reversible, instantaneous desorption has led to the considerable underestimation of the amount of time required to clean up contaminated aquifers using pump-and-treat remediation (Keely, 1989/T14.9). A common pattern observed with organic chemicals is rapid initial desorption of most of the amount followed by a longer period of more gradual desorption. Chen et al. (2002)³⁴ have developed an equation that describes K_d as exhibiting dual-equilibrium desorption behavior that can be used in Equation 4.6 above that may be especially useful for remediation design.

4.5.4 Precipitation

Precipitation reactions, in which geochemical reactions in the aquifer result in a contaminant moving from a dissolved form to an insoluble form, can be an important retardation process for inorganic contaminants. As with adsorption, precipitation reactions are reversible, so it is possible for a contaminant to remobilize if environmental conditions change in the aquifer. Precipitation–dissolution reactions are largely determined by acid–base equilibria and redox conditions (Section 3.4.2). Section 3.2.3 provides additional discussion of precipitation and dissolution reactions. Geochemical distribution-of-species and reaction progress codes (Section 10.3) may help identify important inorganic precipitation reactions.

4.5.5 Transformation

All processes that transform a contaminant retard migration in that the original contaminant will no longer be present. However, unless the contaminant's reaction products are nontoxic inorganic elements, contamination may still persist. Complexation reactions involving heavy metals may even increase toxicity and mobility (Section 3.3.1). Some organic contaminants may be transformed by hydrolysis in ground water, but they often produce intermediate organic compounds of varying toxicity (Section 3.3.2). Microbiological activity is probably the most important means by which contaminants are transformed in the subsurface. Oxidation–reduction reactions (Section 3.3.3) and biotransformation (Section 3.3.4) are probably the two transformation processes that are most significant for most organic contaminants. Section 3.5.4 discusses biotransformation of organic contaminants in more detail.

4.6 PHASE PARTITIONING TO ASSESS PRESENCE OF DNAPLS IN THE SUBSURFACE

As noted in [Section 4.4.4](#) and the next chapter (Section 5.1.4), the subsurface distribution of dense nonaqueous phase liquids is especially difficult to delineate. In the vadose zone, where four

³⁴ Chen, W., A.T. Kan, C.J. Newell, E. Moore, and M.B. Tomson. 2002. More Realistic Soil Cleanup Standards with Dual-Equilibrium Desorption. *Ground Water* 40:153–164.

phases are present (solid, air, water, and DNAPL), the partitioning between the liquid and solid phases is determined by the distribution coefficient (K_d — see [Section 4.5.2](#)) and the partitioning to the soil air is determined by Henry's constant (K_h). In the saturated zone (no gaseous phase present) partitioning will be determined only by the K_d . These phase partitioning relationships can be useful for interpreting soil and soil–gas data for potential presence of DNAPLs. Any time phase partitioning relationships indicate that soil water concentration is greater than the solubility in water, the presence of DNAPL can be inferred.

4.6.1 Soil Water Concentrations from Total Soil Concentrations

Feenstra et al. (1991)³⁵ presented the phase partitioning equation for determining soil water concentration from total soil concentration:

$$C_{sw} = (C_s * bd) / (K_d * bd + S_w + K_h * S_a) \quad (4.8)$$

where:

C_{sw} = soil water concentration

C_s = total soil concentration

bd = bulk density (g/cm^3)

K_d = distribution coefficient

S_w = soil water content

K_h = Henry's constant (gas–water partition coefficient)

S_a = soil air content = (porosity – S_w)

K_d and K_h are properties of the chemical, and bulk density and air- and water-filled porosity are properties of the soil. As an example, carbon tetrachloride ($K_d = 0.4$, $K_h = 0.94$) would require a total soil concentration of 480 mg/kg for soil water concentration to equal solubility. This is less than half the EPA general guideline of 10,000 mg/kg for inferring DNAPL presence (Section 5.1.4), showing the value of using chemical-specific phase partitioning properties. Appendix E includes some more fully worked examples using Equation 4.8.

4.6.2 Soil Water Concentrations from Soil Gas Concentration

Rong (1996),³⁶ using the same basic partitioning theory, developed equations for estimating total soil concentration from soil gas concentration:

$$C_s = C_g * [S_w + (n - S_w) * K_h + bd * K_d] / (bd * K_h) \quad (4.9)$$

where:

C_g = soil gas concentration

n = porosity

Other factors are as defined in Equation 4.8. Once total soil concentration has been calculated, soil water concentration can be calculated using Equation 4.8. Equation 4.9 should be used with caution, because soil gas concentration measurement methods are not very well standardized and can vary considerably when taken from the same location at different times. If a measured gas concentration results in an estimated total soil concentration that exceeds soil water solubility using Equation 4.8, the presence of DNAPL could be inferred. However, it would be preferable to collect an actual soil sample from the location of the soil gas measurement to provide confirmation.

³⁵ Feenstra, S., D.M. Mackay, and J.A. Cherry. 1991. A Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples. *Ground Water Monitoring Rev.* 11(2):128–136.

³⁶ Rong, Y. 1996. How to Relate Soil Matrix to Soil Gas Samples. *Soil and Groundwater Cleanup*, June–July, pp. 20–23.

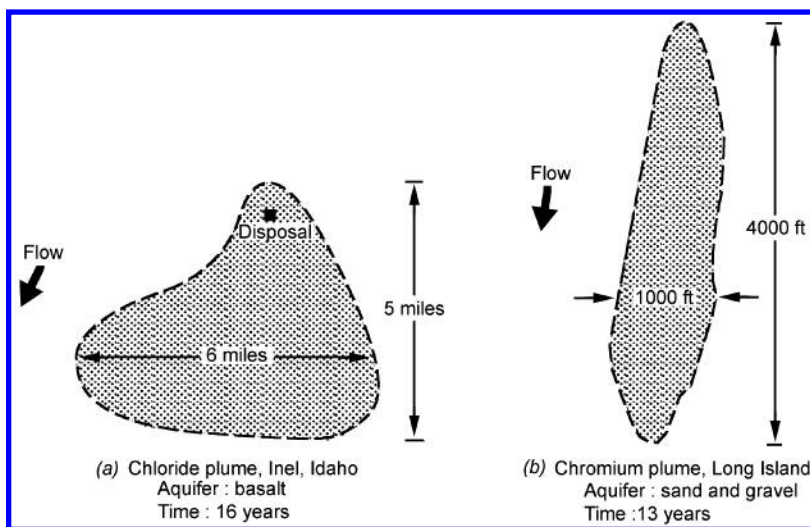


Figure 4.13 Effect of differences in geology on shapes of contamination plumes (Miller, 1985).

4.7 CONTAMINANT PLUME BEHAVIOR

The physical mechanisms of advection and dispersion, as well as a variety of chemical and microbial reactions, interact to influence the movement of contaminants in ground water. The degree to which these mechanisms influence contaminant movement depends on a number of factors, including geologic material properties, pH and Eh, leachate composition, and source characteristics.

4.7.1 Geologic Influences

The rate of ground-water movement is largely dependent on the type of geologic material through which it is moving. More rapid movement can be expected through coarse-textured materials such as sand or gravel than through fine-textured materials such as silt and clay. The physical and chemical composition of the geologic material is equally important. Fine-textured materials with a high clay content tend to impede contaminant migration both by having a low hydraulic conductivity and through ion exchange and physical adsorption. Figure 4.13a illustrates the effect of fracture flow on a chloride plume. Basalt rock has a very low permeability, but fractures allowed movement of the plume a distance of 5 mi downgradient from the source in a period of just 16 years. It is evident that the main orientation of the fractures runs across the direction of ground-water flow because the plume is 6 mi wide. Figure 4.13b shows a chromium plume in a sand and gravel aquifer. This plume moved 4000 ft downgradient from the source with a maximum width of 1000 ft after 13 years. Such a plume is indicative of a relatively homogenous isotropic aquifer. The illustration of time-of-travel calculations in Section 2.6.5 showed that ground water in a sand and gravel aquifer might typically take about 6 years to go a mile. Since the chromium plume traveled less than a mile in 13 years, it is apparent that sorption and possibly precipitation have reduced contaminant movement in this aquifer to about half of what would have been expected without retardation.

4.7.2 pH and Eh

The pH and Eh of the geologic materials and the waste stream strongly influence contaminant mobility. The pH affects the speciation of many dissolved chemical constituents, which in turn determines solubility and reactivity. Ion exchange and hydrolysis reactions are also particularly

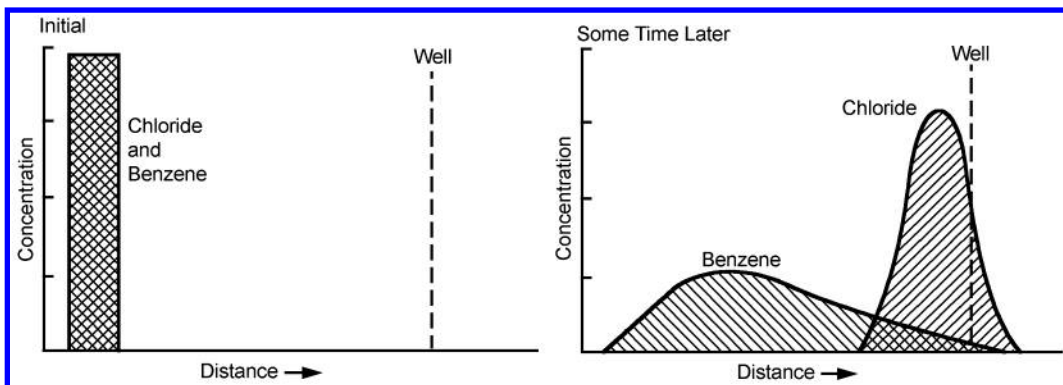


Figure 4.14 Benzene and chloride appearance in a monitoring well (U.S. EPA, 1987a, after Geraghty and Miller, 1985).

sensitive to pH. Eh influences many precipitation and dissolution reactions, particularly those involving iron and manganese, and determines in large measure the type of biodegradation that occurs. Sections 3.4.1 and 3.4.2 discuss the significance of pH and Eh in more detail.

4.7.3 Leachate Composition

The influence of all other factors on contaminant migration ultimately depends on the composition of the leachate or contaminants entering the ground-water system. Similar contaminants may behave differently in the same environment due to the influence of other constituents in a complex leachate. Solubility (which affects the mobile concentration), density, chemical structure, and many other properties can affect net contaminant migration. For example, Figure 4.14 illustrates the appearance of two chemicals, benzene and chloride, in a monitoring well. Even though both contaminants may have entered the ground-water system at the same time and in the same concentration, their detection in the monitoring well reveals significantly different migration rates. Chloride has migrated essentially unaffected, while benzene has been retarded significantly.

4.7.4 Source Characteristics

Source characteristics include the type of source ([Section 4.2.2](#)), the source mechanism ([Section 4.3](#)), and temporal features. Temporal characteristics include the manner in which a contaminant is released over time and the time elapsed since the contaminant's release.

[Figure 4.15](#) presents the effects caused by changes in the rate of a point waste discharge on plume size and shape. *Plume enlargement* results from an increase in the rate of waste discharge to the ground-water system. Similar effects can be produced if the retardation capacity of the geologic materials is exceeded, or if the water table rises closer to the source, causing an increase in dissolved constituent concentration. Decreases in waste discharge, lowering of the water table, retardation through sorption, and reductions in ground-water flow rate can *diminish* the size of the plume. *Stable* plume configurations suggest that the rate of waste discharge is at a steady state with respect to retardation and transformation processes. A plume will *shrink* in size when contaminants are no longer released to the ground-water system and a mechanism to reduce contaminant concentrations is present. Unfortunately, many contaminants, particularly complex chlorinated hydrocarbons and heavy metals, may persist in ground water for extremely long periods without appreciable transformation. Lastly, an intermittent or seasonal source can produce a *series* of plumes that are separated by the advection of ground water during periods of no contaminant discharge.

When contamination comes from a point source, concentrations are typically highest near the source. Non-point sources of contamination, such as from agricultural chemicals, tend to result in

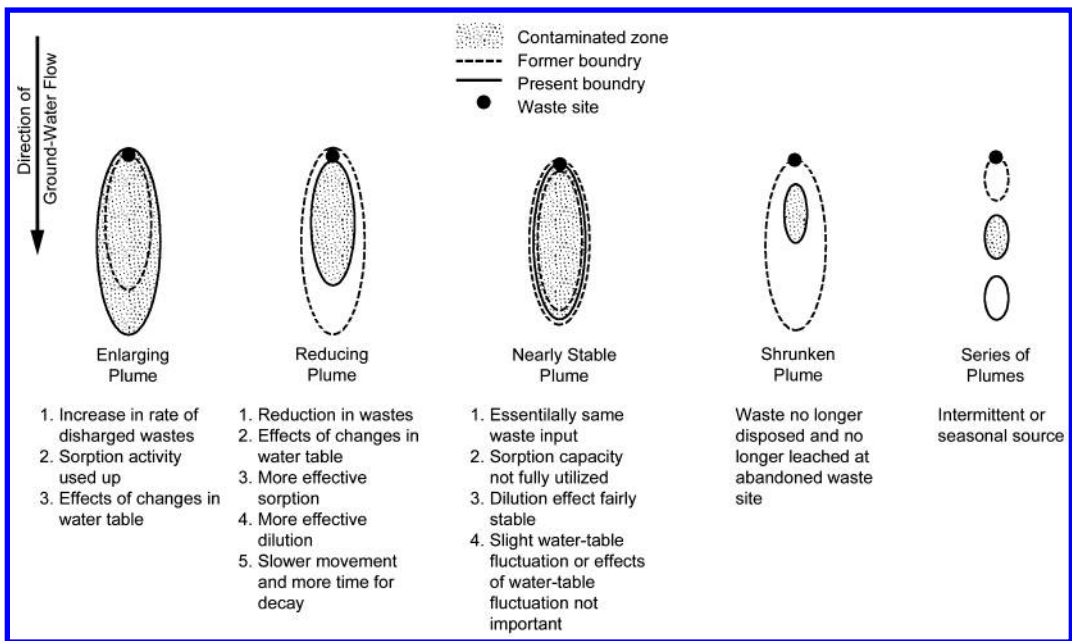


Figure 4.15 Changes in plumes and factors causing the changes (U.S. EPA, 1987a, after U.S. EPA, 1977, and LeGrand, 1965).

relatively low concentrations of contaminants distributed over a relatively large area. In this situation, plumes with distinctive boundaries are less easily defined.

4.7.5 Interactions of Various Factors on Contaminant Plumes

The various factors discussed above can result in varying sizes and shapes of contaminant plumes. Figure 4.16 shows 18 different types of contaminated zones. An *x* marks the contaminant source in each example. Table 4.3 explains the relative importance of dilution, degradation, and

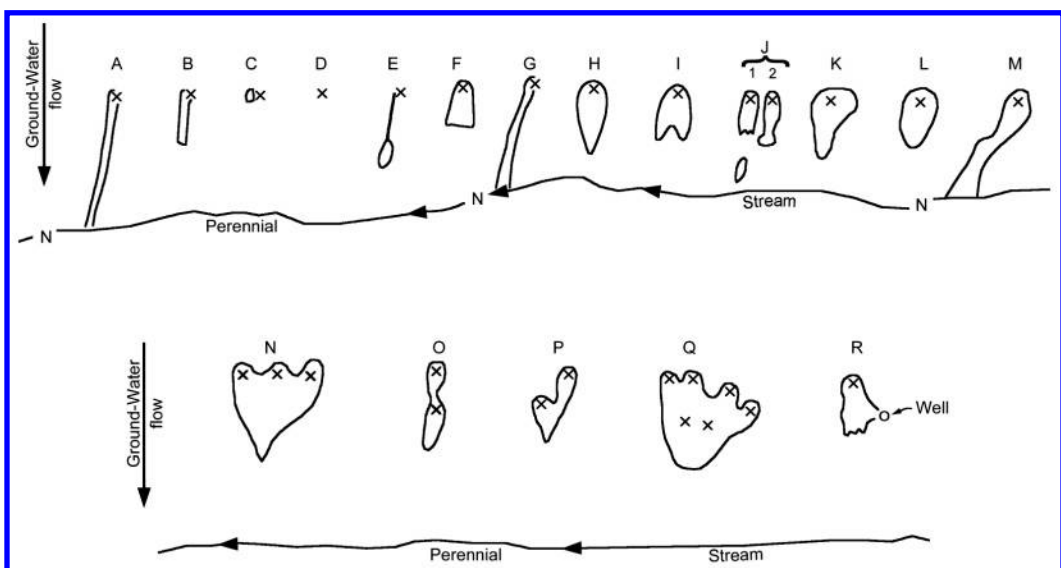


Figure 4.16 Map view of various types of contaminant plumes (LeGrand, 1965).

Table 4.3 Explanation of Contaminant Plumes Shown in Figure 4.16

Site	Contaminant Dilution	Governed by		Liquid Waste Recharge Forming Water Table Mound	Composite Waste Sites	Examples of Type of Contaminant	Remarks
		Plume Decay	Sorption				
A	Not appreciable in ground; some in stream	No	No	No	No	Chlorides, nitrates	
B	Not appreciable	Either decay or sorption or both	No	No	—		
C	Improbable	Perhaps	Perhaps	No	No	Sewage, radioactive wastes	Probably small waste release or good attenuation in zone of aeration
D	No plume formed (see remarks)	Either decay or sorption or both	—	No	No	Sewage, radioactive wastes	Contaminant is completely attenuated in zone of aeration and does not reach zone of saturation
E	Slight near waste site; some at greater distance	Possibly	Possibly	No	No	—	Lack of dispersion near waste site typical of linear openings in rock; contaminated water downgradient disperses into different type of material
F	Yes, suggestive of nearly homogeneous porous materials	Improbable	Improbable	No	No	Chlorides, nitrates	
G	Not appreciable in ground; some near and in stream	Not appreciable	Not appreciable	No	No	Chlorides, nitrates	Irregularities in permeability cause deviation in plume

H	Yes, suggestive of nearly homogeneous porous material	Probably either decay or sorption or both	No	No	Sewage, radioactive wastes		
I	Yes	Perhaps	Perhaps	No	No	—	Downgradient split in plume may be due to dense impermeable rock or great increase in sorptive materials
J	Slight	Not appreciable	Probably not appreciable	No	No	Chlorides, nitrates	Downgradient plume is due to discharge of contaminant to land surface at a surface seep and reinfiltration of contaminant
K	Yes, suggestive of nearly homogeneous porous materials	Either decay or sorption or both		Yes, forming a water table mound	No	Sewage, radioactive wastes	Irregularities in plume caused by changes in permeability or sorption
L	Yes, suggestive of nearly homogeneous materials	Either decay or sorption or both		Yes, forming a water table mound	No	Sewage, radioactive wastes	
M	Some in ground and stream	Not appreciable	Not appreciable	Yes, forming a water table mound	—	Chlorides, nitrates	Deviation in plume due to impermeable zone
N	Yes	Either decay or sorption or both		Yes, forming a water table mound	No	Sewage, radioactive wastes	Contaminated water from three waste sites at right angles to ground-water flow, merging to form a composite plume
O	Yes	Either decay or sorption or both		No	Yes	Sewage, radioactive wastes	Contaminated water from two waste sites parallel to ground-water flow, forming a composite plume

Table 4.3 Explanation of Contaminant Plumes Shown in Figure 4.16 (*Continued*)

Site	Contaminant Dilution	Governed by		Liquid Waste Recharge Forming Water Table Mound	Composite Waste Sites	Examples of Type of Contaminant	Remarks
		Plume Decay	Sorption				
P	Some	Either decay or sorption or both		No	Yes	Sewage, radioactive wastes	Contaminated water from two waste sites at an angle with ground-water flow, forming a composite plume
Q	Some	Either decay or sorption or both		No	Yes	Sewage, radioactive wastes	Large composite plume formed by several waste sites
R	Yes	Either decay or sorption or both		No	No	Sewage, radioactive wastes	Pumping well draws plume toward it; contaminated water is greatly diluted at well

Source: Adapted from LeGrand (1965).

sorption in each plume and lists examples of the types of contaminants typically involved. A few minutes spent examining this figure and the accompanying text in [Table 4.3](#) should give a good feeling for types of interactions between contaminant sources and geology that can be looked for in the field. Contaminant plumes where contamination moves *upgradient* from the direction of ground-water flow are a special type that is not identified in Table 4.3. [Figure 4.10](#) illustrates this for a DNAPL. This can also occur with LNAPLs, such as gasoline, when vapors that have moved in the vadose zone to areas where the saturated zone is upgradient of the source are then transported to the ground water by dissolution or entrainment by percolating water.

4.8 GUIDE TO MAJOR REFERENCES

[Table 4.4](#) provides an index to major references on types and sources of contamination in soil and ground water. The table includes the following major categories: (1) general references on ground-water contamination; (2) sources of information on baseline chemistry that may be useful for evaluating contaminant concentrations; (3) reviews of types of contaminants; (4) national, regional, and specific-source contamination assessment; and (5) general and specific references of contamination sources.

As discussed in [Section 4.2.2](#), the number of potential ground-water contaminants is far too large to provide any detailed discussion of the chemical characteristics of specific contaminants. [Table 4.5](#) provides an index to major references containing more detailed information about specific chemical processes, and chemical characteristics and behavior of contaminants in the subsurface. Generally, only texts, edited volumes, and conference proceedings are indexed in Table 4.5, but some important review papers published in scientific journals are also included. The references include (1) general chemical references, (2) compilations of chemical fate constants, (3) references on ground water and vadose zone/soil chemistry, (4) references on trace elements and heavy metals, (5) references on toxic and other organic chemicals, and (6) references on microbial ecology and biodegradation.

Table 4.4 Index to Major References on Types and Sources of Contamination in Soil and Ground Water

Topic	References
General	Canter and Knox (1987), Cole (1972 — Europe), Guswa et al. (1984), Haimes and Snyder (1986), Meyer (1973), Miller (1980, 1985), Pettyjohn (1972), U.S. Public Health Service (1961), van Duijvenbooden and van Waegeningen (1987), van Duijvenbooden et al. (1981), Ward et al. (1985), Zoller (1994); <u>Bibliographies/Literature Reviews</u> : Bader (1973), Congressional Research Service (1984), Lindorff and Cartwright (1977), Rima et al. (1971), Summers and Spiegel (1974), Todd and McNulty (1974), U.S. EPA (1972), van der Leeden (1991), Zaroni (1971)
Baseline Chemistry	Durfor and Becker (1964); <u>Soil</u> : Connor and Shacklette (1975), Dragun and Chiasson (1992), Ebens and Shacklette (1982), Shacklette et al. (1971a, 1971b, 1973, 1974); <u>Ground/Surface Water</u> : Clarke (1924), Durum and Haffty (1961), Durum et al. (1971), Ebens and Shacklette (1982), Feth (1981), Feth et al. (1968), Fishman and Hem (1976), Hem (1972), Kopp and Kroner (1968), Ledin et al. (1989), Leenheer et al. (1974), Love (1960), Pettyjohn et al. (1979), Skougstad and Horr (1963), Thurman (1985), White et al. (1963, 1970)
Types of Contaminants	Page (1981), Palmer et al. (1988), Pettyjohn and Hounslow (1983), Zoeteman (1985); <u>National Water Quality Assessments</u> : Francis et al. (1981), NAS (1987), U.S. EPA (1985a), Westrick et al. (1984)
Ground Water Contamination Assessments	<u>U.S.</u> : Ballentine et al. (1972), Lehr (1982), Patrick et al. (1987), Pye and Kelley (1984); <u>Regional Assessment</u> : Fuhrman and Barton (1971 — AZ, CA, NV, UT), Miller and Scalf (1974), Miller et al. (1974 — northeast), Miller et al. (1977 — southeast), Scalf et al. (1973 — southcentral), van der Leeden et al. (1975 — northwest); <u>Source Assessments</u> : U.S. EPA (1977 — waste disposal), U.S. EPA (1978, 1983 — surface impoundments), U.S. EPA (1985b — injection of hazardous waste), U.S. EPA (1984 — rural water, 1986a, 1986b — underground storage tanks), U.S. EPA (Pesticides: 1986d, 1990c, 1994)
Contamination Sources	
General	Cape Cod Aquifer Management Project (1988), LaSpina and Palmquist (1992), Meyer (1973), Miller (1982), Noake (1988), Rail (2000), Shineldecker (1992), U.S. EPA (1977, 1987a, 1990b, 1991b), U.S. Fish and Wildlife Service (1986), U.S. OTA (1984)
Contaminant Inventory Guidance	U.S. EPA (1991c); <u>State Guidance</u> : Nebraska Department of Environmental Quality (1992), New Hampshire Office of State Planning (1991), North Dakota State Department of Health (1993), Ohio Environmental Protection Agency (1991), Oregon Department of Environmental Quality (1992), RIDEM (1992), Washington State Department of Health (1993)
Commercial/Industrial	Dotson (1991), U.S. EPA (1990a, 1991a, 1992), Ward et al. (1990), WEF (1993), see also Table 11.6 and references on waste minimization in Table 11.11; <u>Underground Storage Tanks</u> : U.S. EPA (1986a, 1986b); <u>Estimating Chemical Releases</u> : PEI Associates (1990), U.S. EPA (1987b, 1988a, 1990e)
Rural/Nonpoint	Ashton and Underwood (1975), Corwin et al. (1999), Delfino (1977), D'Itri and Wolfson (1987), Nielsen and Lee (1987), Novotny and Chesters (1981), Overcash and Davidson (1980), Ritter and Shirmohammadi (2001), Thornton et al. (1999), U.S. EPA (1984, 1990d, 1991b)
Agricultural Chemicals	Bloom and Degler (1969), Fairchild (1987), Gustafson (1993), Hallberg (1986), Irvine and Knights (1974), Jenkins (1979), Rack and Leslie (1993), U.S. EPA (1986c), USGS (1999), WEF (1993)
Resource Extraction	<u>Energy Production/Use</u> : Boulding (1992), Dotson (1991), U.S. Army Engineers Waterways Experiment Station (1979), U.S. EPA (1988b); <u>Mineral Extraction</u> : U.S. EPA (1985c)
Septic Systems	California Assembly Office of Research (1985), Canter and Knox (1984, 1985), Cartwright and Sherman (1974), Noss (1989), Scalf et al. (1977), Thomson (1984), see also references on bacterial and viral tracers in Table 8.5
Waste Disposal Sites	<u>Landfills</u> : Zaroni (1971), see also landfill gases in Table 12.7; <u>Surface Impoundments</u> : Silka and Swearingen (1978), U.S. EPA (1978, 1983)

Table 4.4 Index to Major References on Types and Sources of Contamination in Soil and Ground Water (*Continued*)

Topic	References
Wells	<u>Abandoned</u> : Aller (1984), Frischknecht et al. (1983), Gass et al. (1977), Texas Water Commission (1989b); <u>Waste Injection</u> : Rima et al. (1971), U.S. EPA (1985b, 1990)
Other Sources	<u>Accidental Spills</u> : Guswa et al. (1984); <u>Military Sites</u> : Kimball et al. (1993)

Table 4.4 References (Appendix F contains references for figure and table sources.)

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* See Preface for information on how to obtain documents from CERL and NTIS. Table 5.3 gives the phone number for the EPCRA Hotline.

Table 4.5 Index to Major References on Contaminant Chemical Characteristics and Behavior in the Subsurface

Topic	References
General Chemical References	ACS (annual), Budavari (1989), Dean (1992), Howard and Meyland (1996), Howard and Neal (1992), Lewis (1992a), Lide (1993), Perry and Chilton (1973), Verschueren (1983); <u>Hazardous Chemicals</u> : ACGIH (1992), Armour (1991), Government Institutes (annual), Keith (1993), Lewis (1990, 1991, 1992b, 1993, 1994), Lucius et al. (1990), NIOSH (1990), Occupational Safety Health Services (1990), Patnalk (1992), Shafer (1993), Shineldecker (1992), U.S. Coast Guard (1985), U.S. DOT (1990), U.S. EPA (1985, 1992a); <u>Agrochemicals</u> : Fisher (1991), James and Kidd (1992), Kamrin and Montgomery (1999), Kearney and Kaufman (1988 — herbicides), Kidd and James (1991), Montgomery (1993), Steinheimer et al. (2000), Walker and Keith (1992)
Chemical Fate Data	Boulding (1990), Callahan et al. (1979), Gherini et al. (1988, 1989), Howard (1989, 1990a, 1990b, 1992a, 1992b, 1993, 1997), Howard et al. (1991), Kollig (1993), Kollig et al. (1991), Lyman et al. (1990, 1992), Mabey et al. (1982), MacKay and Beothling (2000), MacKay et al. (1993, 1995, 1997), Montgomery (1991, 2000), Montgomery and Welkom (1989), Ney (1990), Rai and Zachara (1984), Rai et al. (1984); <u>Sorption/Partition Coefficients</u> : Ellington et al. (1991), Fochman (1981), Howard and Meylan (1992), Leo et al. (1971), Sablić (1988); <u>Henry's Law Constants</u> : Yaws et al. (1991); <u>Hydrolysis Rate Constants</u> : Ellington et al. (1991), Kollig et al. (1990); <u>Diffusion Coefficients</u> : Boynton and Brattain (1929 — gases/vapors), Bruins (1929 — liquids); <u>Speciation</u> : NBS (1981)
Natural Baseline Chemistry	See Table 4.4
Contaminant Sources	See Table 4.4
Chemical/Contaminant Hydrogeology	<u>Texts</u> : Back and Freeze (1983), Bedient et al. (1994), Devinny et al. (1990), Domencio and Schwartz (1998), Fetter (1998), Hounslow (2002 — forensic geochemistry), Kehew (2000), Matthess (1982), Mazor (1990), Palmer (1992), Tinsley (1979), Weber (1972); <u>Papers</u> : Back and Baedecker (1989), Brusseau (1993), Mackay et al. (1985); <u>Subsurface Transport/Retardation Processes</u> : Boulding (1996), Gelhar et al. (1985), Guarmaccia et al. (1992 — multiphase), Güven et al. (1992a, 1992b), Hemond and Fechner-Levy (2000), Huling (1989 — facilitated transport), Kobust and Kinzelbach (1989), Knox et al. (1993), Luckner and Schestakow (1991), Mills et al. (1985), Newell et al. (1995 — LNAPLs), Piwoni and Keeley (1990), U.S. EPA (1989, 1992b), van der Zee and Desouni (1993); <u>DNAPLS Behavior</u> : Huling and Weaver (1991), Pankow and Cherry (1996), Schwille (1988), U.S. EPA (1991)
Vadose Zone/Soil/Sediment Chemistry	Environmental Science and Engineering (1985), Selim and Sparks (2001a), Yaron et al. (1984), Yong et al. (1992); <u>Inorganic Chemicals</u> : Bar-Yosef et al. (1989), Selim and Iskander (1999); <u>Toxic Organic Chemicals</u> : Dragun (1998), Gerstl et al. (1989), Goring and Hamaker (1972), TNO/BMFT (1985, 1989); <u>Contaminated Sediments</u> : Baker (1980), Gambrell et al. (1977), Horowitz (1991), Shear and Watson (1977)
Biodegradation/Contaminant Microbiology	Alexander (1994), Borchardt et al. (1977), Dunlap and McNabb (1973), Fochman (1981), Gibson (1984), Kobayashi and Rittman (1982), Leisinger et al. (1981), Mitchell (1971), Ratledge (1993), Rogers (1986), Rogers and Abramowicz (1993), Scow (1982), Sims et al. (1991), Zehnder (1988), Yong and Cernuiglia (1995); <u>Soil</u> : Huang and Schnitzer (1986), Nelson et al. (1983), Ramsey et al. (1972); <u>Ground Water</u> : Bitton and Gerba (1984), Bouwer and McCarty (1984), Ghiorse and Wilson (1988), Maki et al. (1980), Tabak et al. (1981), Wilson and McNabb (1983)

Table 4.5 Index to Major References on Contaminant Chemical Characteristics and Behavior in the Subsurface (*Continued*)

Topic	References
Trace Elements/Heavy Metals	Beck et al. (1992/T3.12), Bowen (1966), Chappelle and Peterson (1976), Frankenberger (2001 — As), Frankenberger and Benson (1994 — Se), Frankenberger and Engberg (1998 — Se), Hem (1964), Jarrell et al. (1980 — Mo), Kramer and Allen (1988), National Research Council Canada (1976, 1978a, 1978b, 1979a, 1979b, 1981, 1982), Prasad (2000), Purves (1978), Shaw (1989), Thibodeaux (1979), Thornton (1983), Watras and Huckabee (1994 — mercury); <u>Sediment</u> : Gambrell et al. (1977), Horowitz (1991); <u>Soil</u> : Allaway (1968, 1991), Aubert and Pinta (1978), Copenhaver and Wilkinson (1979a), Dotson (1991), Fuller (1977), Gibb and Cartwright (1987), Gobran et al. (2001 — rhizosphere), Huang et al. (1994b), Iskander and Kirkham (2001), Jacob (1989 — selenium), Kabata-Pendias (2001), Kotaby-Amacher and Gambrell (1988), Lisk (1972), McBride (1989), McLean and Bledsoe (1992), Page (1974), Rai and Zachara (1988), Selim and Iskander (1999), Selim and Sparks (2001b), Zachara et al. (1992); <u>Water</u> : Allen et al. (1990, 1993), Förstner and Wittman (1981), Kramer and Duinker (1984), Krenkl (1975), Moore and Ramamoorthy (1984a), Palmer and Puls (1994), Rai and Zachara (1986), Salbu (1994), Salomons and Förstner (1984), Singer (1973), Singh and Subramian (1983); <u>Sewage Sludge/Wastewater</u> : Page (1974), Page et al. (1981); <u>Biogeochemistry</u> : Adriano (1992), Wildung and Drucker (1977)
Inorganic Agricultural Chemicals	<u>Nitrates</u> : Burt et al. (1993), Follet et al. (1991)
Toxic and Other Organic Chemicals	Beck et al. (1994/T3.12), Larson and Weber (1994), Linn et al. (1993), Lyman et al. (1992), NAS (1972), Thibodeaux (1979); <u>Soil</u> : Huang et al. (1994a), Meikle (1972), Minnich (1993 — VOCs), Morrill et al. (1982), Nelson et al. (1983), Overcash (1981), Sawhney and Brown (1989), Yong (2002); <u>Ground/Surface Water</u> : Borchardt et al. (1977), Faust and Hunter (1971), Gerstl et al. (1989), Moore and Ramamoorthy (1984b), Nielsen (1994); <u>VOCs</u> : Wang et al. (1996); <u>Aliphatic Hydrocarbons</u> : Barbee (1994), Britton (1984), Moore and Ramamoorthy (1984b); <u>Halogenated Hydrocarbons</u> : Rogers and Abramowicz (1993), Sims et al. (1991); <u>Monocyclic Aromatic Hydrocarbons and Halides</u> : Chapman (1972), Gibson and Subramian (1984), Moore and Ramamoorthy (1984b), Reinike (1984); <u>MTBE</u> : Jacobs et al. (2000); <u>Phthalate Esters</u> : Pierce et al. (1980), Ribbons (1984); <u>Polycyclic Aromatic Hydrocarbons</u> : Moore and Ramamoorthy (1984b), Safe (1984); <u>Pesticides</u> : Cheng (1990), Cheremisinoff and King (1994), Copenhaver and Wilkinson (1979b), Crosby (1973), Guenzi (1974), Hamaker (1972), Hamaker and Thompson (1972), Haque and Freek (1975), Honeycutt and Schabacker (1994), Kamrin (1997), Kearney and Kaufman (1972), Linn et al. (1993), Moore and Ramamoorthy (1984b), NAS (1972), Ou et al. (1980), Rao and Davidson (1980), Somasundaram and Coats (1991), see also references for agricultural chemicals in Table 4.4; <u>Explosives</u> : Environmental Science and Engineering (1985)

Table 4.5 References (Appendix F contains references for figure and table sources.)

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* See Preface for information on how to obtain documents from CERL and NTIS.

PART II

Assessment and Monitoring

Planning Field Investigations

Well-planned field investigations for assessing soil and ground-water quality or contamination reduce costs and yield better results than investigations that are conducted using a cookbook or haphazard approach. This chapter focuses on the things that should be done before initiating a significant level of fieldwork and reviews some statistical concepts and techniques that are especially important in contaminant investigations. Subsequent chapters cover more specific field methods for local and site investigations:

- Geophysical and remote sensing techniques (Chapter 6)
- Characterization of vadose zone and ground-water hydrology (Chapter 7)
- Soil and ground-water tracers (Chapter 8)
- Field sampling and monitoring (Chapter 9)

5.1 OVERVIEW OF INVESTIGATION PLANNING PROCESS

5.1.1 Investigation Objectives

A clear definition of objectives is the first step in effective planning. The objectives of an investigation will in large measure define the approach and methods that will be used. Some common objectives include:

- *Collection of Baseline Data.* For many years the U.S. Geological Survey (USGS) has collected both quality and quantity data of both surface and ground water. These data are collected to provide historical documentation of changes in amount and quality of ground water, and baseline data on “natural” levels of chemical constituents in ground water.
- *Pollution Prevention.* Field investigations for the siting of waste disposal facilities aid in the selection of areas that are less vulnerable to the effects of contamination and design of measures to prevent contamination. Field investigations of varying intensity are required to delineate drinking water wellhead protection areas and develop management practices to prevent pollution.
- *Regulatory Compliance.* Field investigations and monitoring are required to demonstrate compliance with regulatory standards dealing with underground storage tanks, and waste disposal, storage, or treatment facilities.
- *Litigation and Regulatory Enforcement.* Soil and ground-water investigations often play an important role in litigation. Results may be used to establish liability under the civil laws of trespass or in response to federal legislation such as RCRA and Superfund. In this situation, special attention must be given to documentation of field and laboratory procedures and to use of stringent quality

assurance/quality control (QA/QC) procedures. At the beginning of the study, legal counsel should provide guidance in developing the work plan.

- *Research.* Soil and ground-water quality investigations for research purposes are as varied as the nature of the research itself. Objectives of these investigations range from model validation to determining the rates and breakdown products of contaminant degradation. Such investigations often require specialized field equipment and technologies to obtain representative samples of subsurface materials for use in column and microcosm studies. Usually more observation points are employed in research studies than in other types of ground-water investigations. As with investigations involving litigation or regulatory enforcement, stringent QA/QC procedures must be followed.

A clear statement and understanding of an investigation program's objectives must precede decisions concerning sampling locations, piezometer or well types, numbers, location, depth, constituents of interest, and methods of sample collection, storage, transport, and analysis. Each decision requires consideration of the data needs and associated costs involved in each phase of a site characterization and monitoring program. In general, a phased approach is best, in which experimental design focuses on the reasoning behind each piece of data that is collected, and use of less expensive field methods guides use of more expensive methods as needed. For example, surface geophysical methods and handheld or truck-mounted subsurface probing devices can guide the location of boreholes and the monitoring of well installations using larger drill rigs. In the same way, use of less expensive chemical field screening and analytical techniques on a relatively large number of samples can guide selection of a fewer number of samples for chemical analysis in fixed laboratories (Section 9.6).

5.1.2 Investigation Scale

Soil and ground-water quality investigations can be divided into three general types based on scale or geographic scope: regional, local, and site-specific evaluations.

Regional Investigations. Regional evaluations, which may encompass several hundred or even thousands of square miles, are mainly reconnaissance efforts and are used to obtain an overall evaluation of the ground-water situation. This broad-brush type of investigation can be the starting point for two general types of explorations. The purpose of the first type is to locate potential individual sources or sites of ground-water contamination to determine if a problem exists. The second type aims at determining the occurrence and availability of ground water on a more regional scale. Then, if necessary, the exploration would ascertain prevalent hydrologic properties of earth materials, generalized flow directions in both major and minor aquifers, primary sources and rates of recharge and discharge, chemical quality of the aquifers and surface water, and locations and yields of pumping centers. These data can be useful in more detailed studies because they provide information on the geology and flow direction, both of which impact smaller-scale studies.

Local Investigations. Local investigations are intermediate in scope and areal extent between regional evaluations and site investigations. For example, an investigation of the hydrogeology of an area encompassing a few tens or several hundred square miles in order to evaluate the effect of oil field brine production and disposal would fall short of being called regional. At the other end of the scale, local investigations grade into site investigations when a hydrogeologic assessment must extend beyond the specific boundaries of a site. Investigations of this nature usually include only a few square miles. Their purpose is to define in greater detail the geology and hydrology in an area surrounding a specific site or sites of concern. The information obtained is used in designing and carrying out more detailed site investigations.

Site Investigations. The purpose of the site evaluation is to ascertain, with considerable certainty, the extent of soil and ground-water contamination, its local source or sources, and hydraulic and chemical properties that influence contaminant migration. The site investigation is the most detailed, complex, costly, and, from a legal and restoration viewpoint, most critical of the three

types of field studies. A site investigation must address a large number of pertinent parameters affecting contaminant transport and transformation. These include the soils, geology, hydrogeology, geochemical interactions, biotic and abiotic degradation processes, and the rate of contaminant movement through the unsaturated and saturated zones. All of the phenomena that may influence the movement of contaminant plumes, such as pumping wells, local streams, and multiaquifer interactions, must be characterized.

At the same time, ancillary assessments at the site might include tank inventories, toxicological evaluations, air pollution monitoring, studies of manufacturing and waste handling procedures, as well as many other studies, all of which will eventually interface in the development of a comprehensive site investigation report.

5.1.3 Planning and Conducting Contaminant Investigations

Regardless of the complexity or detail of the investigation, a logical series of steps should be followed. Although each investigation is unique, most investigations include the following steps: (1) definition of objectives, (2) collection of existing data (including literature review), (3) field investigations and sampling, (4) laboratory analysis, (5) data interpretation and conclusions, and (6) report preparation and recommendations. These elements interact iteratively as part of a larger process that is illustrated in [Figure 5.1](#). In contaminant investigations, the term *conceptual site model* is now widely used to refer to the system behavior hypothesis in [Figure 5.1](#).

Failure to follow these steps may result in excessive cost and, in the worst case, rejection of the study results as inadequate. Common mistakes include:

- Failure to define precise objectives appropriate for the purpose and scale of the investigation.
- Failure to review all available data on the site prior to initiating the field investigation. For example, failure to identify off-site sources of ground-water pumping may lead to incorrect interpretations of ground-water flow patterns.
- Failure to obtain necessary basic hydrogeologic data before selecting locations for more intensive water quality sampling. This may result in unnecessary expense in water quality analyses.
- Misinterpretation of the data collected during the investigation.

Developing Study Objectives and a Work Plan. Establishing an investigation's major objectives is essential to a successful and cost-effective project. All interested parties should clearly define and agree upon these points. These objectives should be stated in writing and referred to often during the life of the study. Otherwise, the study may drift from the original objectives, resulting in the costly collection of superfluous information at the expense of other essential information.

The approach, time requirements, and funding can vary greatly between a regional reconnaissance evaluation and a site investigation. The former, which deals with regional properties, may require a relatively short time, while the latter, which necessitates minute detail, may demand years. In either case, the time and resource requirements are dictated by the goals, and the success of the work is measured by how directly the investigation pursues these goals.

For example, a stated objective to "measure the water level surface in a given township using existing wells" indicates the limited nature of the study. On the other hand, an objective to "evaluate the degradation rate of tetrachloroethylene at a specific spill site, define the plumes of the parent and degradation contaminants, and predict the location and concentrations of these contaminants in 10 years" clearly requires a substantial level of effort. The investigation would require a detailed knowledge of the site's soils, geochemistry, geology, and hydrogeology, along with sophisticated analytical capabilities, predictive models, and the information necessary to drive them.

A *work plan* provides the overall administrative framework for an investigation and should be responsive to the stated objectives, using existing data and information to the fullest extent possible. The field portion of an investigation is guided by a more specific *sampling and monitoring plan* and a *health and safety plan*. Data quality assurance and quality control can be addressed in a

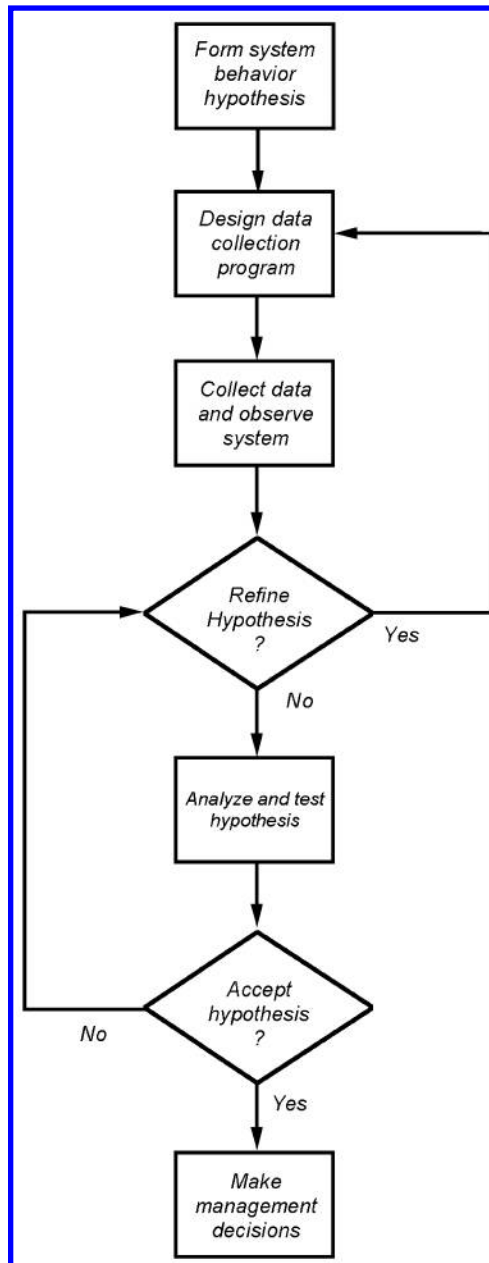


Figure 5.1 Site characterization phases (Mercer and Spalding, 1991a, after Bouwer et al., 1988).

separate *QA/QC plan* or in the appropriate section of the work plan and sampling and monitoring plan. [Section 5.3](#) addresses more specific aspects of developing a sampling and monitoring plan, including QA/QC. Health and safety issues are addressed further in Section 12.2.6.

Unlike the project goals, which are fixed, the work and the sampling and monitoring plans need to be flexible. For example, the position of all test wells, and boring and monitoring points cannot be determined at the start of an investigation. Rather, these locations should be adjusted on the basis of information obtained as each hole is completed. In this way, the usefulness of the data obtained from each drill site can be maximized, and future sampling points located to increase understanding of the ground water and the contamination situation at the site under study.

Similarly, the contaminants of interest, appropriate analytical methods, details of sampling techniques, and the required number of samples cannot be accurately estimated at the beginning of a project. These must be refined as data are collected and their results interpreted.

A work plan may need to incorporate procedures or guidelines established by EPA, such as the RCRA Ground Water Monitoring Technical Enforcement Guidance (U.S. EPA, 1986; 1993/T9.10), and provisions for the safety and health of workers at the site (NIOSH/OSHA/USCG/EPA, 1985/T12.7). State regulatory agencies may have even more stringent requirements. Also, in the case of Superfund and RCRA sites, investigators will probably need to coordinate with and use data collected by consultants for potentially responsible parties (PRPs).

Existing Data Collection. The amount of existing data will affect the sophistication of the preliminary conceptual site model. Knowledge of site history and the location of anthropogenic features such as buried cables and pipelines is also essential for worker health and safety when field investigations begin. When feasible, a preliminary or reconnaissance site visit provides a basis for evaluating the quality of existing data as it applies to the specific area of interest. [Section 5.2](#) addresses existing information sources in some detail.

Field Investigation. The initial field phase of a ground-water investigation is the most intensive and important part of the project, and the data collected during this phase will determine the project's success. Some of the main factors affecting the quality of field data collected include an understanding of the basic geology and hydrogeology of the site (Chapters 1 and 2), well and aquifer testing (Section 7.3), a knowledge of the types of contaminants involved and their behavior in the subsurface (Chapters 3 and 4), the appropriate use of geophysical methods (Chapter 6), the location and construction of monitoring wells (Section 9.3), and the sampling and analytical techniques (Chapter 9). Tracer tests (Chapter 8) may also provide valuable data.

In the late 1980s there was a general recognition that a lot of money was being wasted in contaminant investigations, especially at uncontrolled hazardous waste sites that had been targeted for action under EPA's Superfund program. Tens of thousands of dollars were being spent on expensive chemical analysis of ground-water samples taken from monitoring wells that were placed without a good understanding of the hydrogeology of a site. Figure 5.2 provides a qualitative illustration of the longer-term cost savings that result from increasingly intensive site characterization efforts. [Table 5.1](#) identifies the types of site characterization activities associated with the conventional, state-of-the-art, and state-of-the-science approaches, along with the advantages and

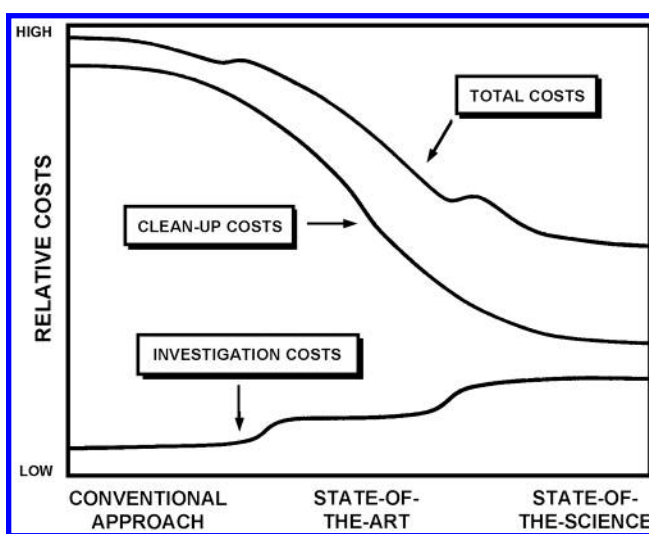


Figure 5.2 General relationship between site characterization costs and cleanup costs as a function of the characterization approach (Keely, 1987).

Table 5.1 Comparison of Approaches to Site Characterization Efforts

Approach	Advantages	Disadvantages
Conventional		
<ul style="list-style-type: none"> • Install a few dozen shallow monitoring wells • Sample and analyze numerous times for 129+ pollutants • Define geology primarily by driller's log and cuttings • Evaluate hydrology with water level maps only • Possibly obtain soil and core samples (chemical extractions) 	<ul style="list-style-type: none"> • Rapid screening of problem • Moderate costs involved • Field and lab techniques standardized • Data analysis relatively straightforward • Tentative identification of remedial options possible 	<ul style="list-style-type: none"> • True extent of problem often misunderstood • Selected remedial alternative may not be appropriate • Optimization of remedial actions not possible • Cleanup costs unpredictable and excessive • Verification of compliance uncertain and difficult
State of the Art		
<ul style="list-style-type: none"> • Conduct geophysical surveys (resistivity soundings, etc.) • Install depth-specific piezometers and well clusters • Sample and analyze for 129+ pollutants initially • Analyze selected contaminants in subsequent samples • Define geology by extensive coring/split-spoon samples • Evaluate hydrology with well clusters and geohydraulic tests • Perform limited tests on solids (grain size, clay content) 	<ul style="list-style-type: none"> • Conceptual understanding of problem more complete • Better prospect for optimization of remedial actions • Predictability of remediation effectiveness increased • Cleanup costs lowered; estimate improved • Verification of compliance soundly based, more certain 	<ul style="list-style-type: none"> • Characterization costs somewhat higher • Detailed understanding of problem still difficult • Full optimization of remedial actions not likely • Field tests may create secondary problems • Demand for specialists increased
State of the Science		
<ul style="list-style-type: none"> • Assume state-of-the-art approach as starting point • Conduct tracer tests and borehole geophysical surveys • Determine percent organic carbon, exchange capacity, etc., of solids • Measure redox potential, pH, dissolved oxygen, etc., of fluids • Evaluate sorption-desorption behavior using select cores • Identify bacteria and assess potential for biotransformation 	<ul style="list-style-type: none"> • Thorough conceptual understanding of problem obtained • Full optimization of remedial actions possible • Predictability of remediation effectiveness maximized • Cleanup costs lowered significantly; estimates reliable • Verification of compliance assured 	<ul style="list-style-type: none"> • Characterization costs significantly higher • Few previous field applications of advanced theories • Field and laboratory techniques not yet standardized • Availability of specialized equipment low • Demand for specialists dramatically increased

Source: Adapted from Keely (1987).

disadvantages. As of the mid-1990s, the conventional approach has moved closer to the state-of-the-art defined in Table 5.1.

Data Analysis and Conclusions. Data interpretation should begin with the development of the work plan. Even at a moderate-size site, a ground-water investigation of limited scope can result in the collection of a great deal of data. The time loss and frustration avoided during data interpretation are directly proportional to the degree to which the study anticipates (1) the types and amounts of data collected; (2) the calculations required to determine contaminant transformation process rates, support conclusions, and make projections; (3) the correlations required to prove cause and effect, define relationships, and determine reaction coefficients; and (4) the graphic displays needed for reports and presentations.

To the extent possible, the amounts and types of data should be anticipated early in the project and provisions made for the continuous input of collected information as the work progresses. The

widespread availability and use of computers greatly facilitates data processing, and software exists for a wide variety of data handling requirements (Section 10.5). The QA/QC program should include the data handling system so that data quality can be monitored.

If predictive models are required at some point in the investigation, or later in the development of an aquifer remediation project, they should be formulated or selected from basic flow and transport models as early as possible (Section 10.4). Then requirements for acquisition of the appropriate data can be built into the project plan. Steps should also be taken for model calibration and validation as the project proceeds.

The groundwork for the development of conclusions also should be laid in the early stages of the project by establishing hypotheses pertaining to the project objectives. The project should be designed and modified around their acceptance or rejection. If done correctly, this approach ensures that the project design responds efficiently to the project goals and minimizes the collection of extraneous information.

5.1.4 Special Considerations for DNAPL Investigations

Sites contaminated by dense nonaqueous liquids (DNAPLs) present special challenges for contaminant distribution characterization, especially when the amount spilled is enough to move through the saturated zone and form a pool of free product at the bottom of an aquifer (see Figure 4.10c). Also, the tendency of DNAPLs to move through the vadose and saturated zones as fingers rather than as a uniform wetting front means that direct sampling may miss the presence of free product or areas of residual saturation. Cohen and Mercer (1993/T9.10) and U.S. EPA (1992c/T9.10) provide detailed guidance on techniques for direct detection of DNAPLs. These include using NAPL–water interface probes that signal a change in conductivity of the borehole fluid, inspecting fluid retained on a weighted cotton string lowered down a well, pumping and recovering fluid, and using transparent bottom-loading bailers. Methods to confirm DNAPLs in soil samples include shaking soil samples in a jar with water to separate DNAPLs from the soil and pouring water through soil in a funnel with a filter paper and examining the filter for separate phases. As described in Section 8.3.5, alcohol partitioning tracers can be used to quantify the amount of residual DNAPLs in the subsurface. Kram et al. (2001, 2002)¹ provide a good summary of approaches and costs of DNAPL characterization methods. Although there have been significant advances in the last 10 years in methods for characterizing the extent of DNAPL contamination, there is still considerable difference of professional opinion concerning the best approaches to remediation of DNAPL contaminated sites.²

Guidelines for inferring DNAPL presence from chemical tests include:

- Dissolved concentrations of DNAPL chemicals in ground water are greater than 1% of pure phase solubility or effective solubility when mixtures are present. Griffin and Watson (2002)³ found that this guideline was useful for defining a DNAPL study area where more direct detection methods are used.
- Concentrations of DNAPL chemicals on soils are greater than 10,000 mg/kg (equal to 1% soil mass). See below for chemical-specific refinement of this criterion using partitioning theory.
- Soil concentrations indicate soil water concentrations greater than the pure phase solubility based on soil phase partitioning relationships (see Section 4.6.1).
- Organic vapor concentrations detected in soil gas exceed 100 to 1000 ppm. See Section 4.6.2 for chemical-specific refinement of this criterion using partitioning theory.

¹ Kram, M.L., A.A. Keller, J. Rossabi, and L.G. Everett. 2001. DNAPL Characterization Methods and Approaches, Part 1: Performance Comparisons. *Ground Water Monitoring and Remediation* 21(4):109–123. Part 2: Cost Comparisons. 22(1):46–61, 2002.

² Jackson, R.E. 2001. DNAPL Remediation: Which “New Paradigm” Will Prevail? *Ground Water Monitoring and Remediation* 21(3):54–58.

³ Griffen, T.W. and K.W. Watson. 2002. A Comparison of Field Techniques for Confirming Dense Nonaqueous Phase Liquids. *Ground Water Monitoring Review* 22(2):48–59.

Nyer (1999)⁴ points out that dense *aqueous* phase liquids (DAPLs) can also sink to the bottom of an aquifer, although they are less common and have received less attention in the chemical contaminant literature. Salt water entering a freshwater aquifer will behave as a DAPL.

5.1.5 Accelerated/Expedited Site Characterization Approaches

The conventional or traditional approach to characterizing contaminated sites involved multiple mobilizations for such tasks as geophysical measurements, soil sampling, installation of monitoring wells, and ground water sampling. Typically the project leader is in the office and junior staff are in the field, with the location and number of soil or ground water samples determined beforehand. Data analysis and interpretation is usually accomplished in the office weeks to months after fieldwork, and multiple reports are generated for the results of different mobilizations.

The decade of the 1990s saw the development of a number of more rapid approaches to site characterization. These approaches have been called by different names (see Table 9.10 for full citations), but share many common elements: expedited site characterizations (Burton et al., 1993; ASTM D6235), accelerated site characterization (ASTM E1912), STERDI — Simultaneous Testing, Exploration, Remedial Design, and Installation (Waslenchuk and Man, 1996), adaptive sampling (Robbat, 1997), rapid site assessment (Applegate and Fitton, 1997), and dynamic field activities (U.S. EPA, 2003).

A number of relatively recent technological developments have encouraged the development of expedited site characterization approaches.

- *Advances in Noninvasive and Minimally Invasive Technologies.* Improvements in instruments and signal processing have reduced the cost and turnaround time for data interpretation for a variety of surface and borehole geophysical methods. Similar advances have occurred for direct-push soil and ground water sampling equipment, and by adaptation and enhancement of standard geotechnical cone penetration technology (see Section 6.5).
- *Advances in Chemical Field and Laboratory Technologies.* Improvements and miniaturization of standard laboratory chemical analytical instruments, including automation of sample analyses and improvements in software for analyzing instrument signals, together with the development of a wide variety of field chemical test kits for environmental contaminants, make “real time” (minutes to days) sample data results available during a single mobilization for three-dimensional mapping of subsurface contamination. Mobile laboratories or the use of overnight delivery to fixed laboratories means that there are essentially no limits on the quality of chemical data that can be used for on-site technical decision making.
- *Advances in Data Analysis and Management Technologies.* Miniaturization and increased computing power, along with the availability of a wide range of software for environmental data management, visualization, and analysis, make field data compilation, reduction, and interpretation possible.

Common elements to the various expedited site characterization approaches include (1) a dynamic or flexible work plan that allows the number and location of samples to be determined using on-site decision making based on the results of previous samples, (2) a limited number of mobilizations (usually one or two), (3) the use of highly experienced personnel in the field, and (4) the use of site characterization and chemical sampling and analysis methods that provide a rapid turnaround time to support on-site decision making.

American Society for Testing and Materials (ASTM) has developed standards for expedited site characterization of hazardous waste contaminated sites (ASTM D6235) and for accelerated characterization for confirmed or suspected petroleum releases (ASTM E1912). The U.S. Environmental Protection Agency is encouraging use of similar approaches through its Triad campaign

⁴ Nyer, E.K. 1999. DNAPL: Stop the Madness. *Ground Water Monitoring and Remediation* 19(1):62–66.

(EPA 2001c/T9.10). The Triad campaign promotes the use of systematic planning, dynamic work plans, and quick turnaround measurements for streamlining site activities.

The EPA Dynamic Field Activities Guidance (EPA 2003/T9.10) addresses site characterization, cleanup, and treatment system optimization and includes case studies for each application. The cost savings, compared to traditional approaches, ranged from 15 to 57%, while the time savings ranged from 33 to 60%.

5.2 EXISTING INFORMATION SOURCES

Before fieldwork begins in earnest, available information about the area of interest should be obtained and reviewed. This includes first reviewing published maps and reports about soils, geology, and hydrology of the area. The next step is finding and analyzing any unpublished data, such as well drill logs, and hydrologic and water quality data on file at local, state, or federal government offices. EPA's STORET and USGS's National Water Data Exchange (NAWDEx) databases may have ground-water quality data from the area (see [Table 5.13](#)). Finally, examination of aerial photographs provides an opportunity to relate knowledge gained in reviewing published and unpublished information to the specific wellhead area, and helps focus field efforts to collect additional required information.

The above steps do not have to be followed in strict sequential order, but an intensive initial effort to identify and review published and other existing information will generally pay off by (1) avoiding field effort spent in collecting data that is already available, and (2) targeting the location and type of field data collection to yield the greatest benefits. [Table 5.2](#) identifies major potential sources of information, and [Table 5.3](#) provides a list of major EPA information hotlines, information numbers, and electronic databases.

Getting to know one or more individuals in the various state and federal agencies that publish and maintain files of information on soils, geology, and water resources can facilitate the process of determining what is available for the area of interest. The planning and utility departments of local government are also sources of potentially valuable information that may not be available from other sources. Worksheet D-W2 provides a form for listing personal contacts and identifying available maps that can provide a starting point for compiling a hydrogeologic map of an area.

5.2.1 Soil and Geomorphic Data

Soil maps can be used as an aid in geologic interpretation because soil types are often related to both the original rock and the weathering processes from which they were derived. Soil information is also necessary to evaluate the potential for movement of organic and inorganic compounds through the unsaturated zone.

Section 7.4.1 discusses the use of soil survey data in the estimation of aquifer parameters. Soil surveys published by the Soil Conservation Service (SCS) of the U.S. Department of Agriculture are typically at a scale of 1:15,840 or 1:20,000 and mapped on an air photo base. Simplified geomorphic maps can be readily developed from a soil map by grouping soil map units into larger geomorphic units (floodplains, terraces, uplands, etc.). Nonfloodplain soils are differentiated on the basis of slope with letter designations in the map symbol. This allows development of geomorphic units based on slope range. Slope range, combined with the infiltration characteristics of the soil, allows qualitative interpretations of infiltration runoff characteristics of an area (see, for example, index surface runoff classes in [Table 2.1](#) of Boulding (1994/T9.10).

5.2.2 Geologic and Hydrologic Data

Geologic reports, maps, and cross sections provide details of the surface and subsurface, including the areal extent, thickness, composition, and structure of rock units. Geology and hydro-

Table 5.2 Sources and Types of Existing Data for Soil and Ground Water Quality Investigations

Sources	Types/Comments
Cross-Cutting Information Sources	
Remote sensing imagery	Drainage patterns, land use, vegetation stress, historical land development, and geologic structure; see ASTM D5518 (Table A.14)
Computer databases	Wide variety of reference data and bibliographies; see Table 5.13
U.S. EPA and State Environmental Agency	
RCRA permits and applications	EPA identification numbers
Waste generators and transporters	Generator annual reports; may require special clearance for reviewer
NPDES permits and applications	Liquid waste types; treatment processes; production information
Uncontrolled waste disposal sites	
Spills of oil and hazardous materials	
Water supplies	Nearest water supply
Enforcement actions	Problem history; previous findings
Surveillance reports	Plans, concerns, and past problems
Other Federal Agencies	
U.S. Geological Survey	Technical geologic and hydrologic reports, maps, aerial photographs, and water monitoring data
U.S. Department of Agriculture (ASCS, SCS)	Soil maps, types, physical characteristics, depths association, and uses
U.S. Fish and Wildlife Service	Endangered species
National Oceanic and Atmospheric Administration (NOAA)	Climatic data
National Ocean Survey	Tidal data, historic, recent, and projected
Land Management Agencies (BIA, BLM, Forest Service)	Air photos, vegetation/land use maps, hydrologic data
Occupational Safety and Health Administration (OSHA)	Processes, hazards, protective equipment needs
Other State Agencies	
Geological Survey	Technical geologic and hydrologic reports, state geologic maps, and monitoring data
Water Division/Survey	Well locations and logs
Regional Planning Agencies	
CWA-Section 208 Agency	
Other	Areawide solid waste/wastewater treatment management
County Offices	
Health Department	Problems, complaints, analytical results
Planning and zoning	Land use restrictions
Assessor	Plant maps and land owners
Surveyor	Survey benchmark locations
City Offices	
Chamber of Commerce	Information and local industries, including number of employees, principal products, and facility addresses
Clerk	
Engineer	Foundation and inspection reports; survey benchmark locations
Fire department	History of fires or explosions at facility
Law enforcement	Complaints and violations of local ordinances
Water and sewer	Location of buried mains and lines

Table 5.2 Sources and Types of Existing Data for Soil and Ground Water Quality Investigations (*Continued*)

Sources	Types/Comments
	Company Files and Records
	Confidential records require special handling and storage
	Contractors
Building	Local soils, geology, and shallow water levels
Soil/foundation, water well drillers	Local soils, geology, hydrogeology, water levels, regulations, and equipment availability
	Utility Companies
Gas	Location of buried lines
Electric	
Water	
Petroleum or natural gas pipelines	

Source: Adapted from Sisk (1981).

Table 5.3 Environmental Hotlines, Clearinghouses, and Electronic Databases

General
National Service Center for Environmental Publications: 800-490-9198; < www.epa.gov/ncepihom/ >
EPA/OPPT/Pollution Prevention Information Clearinghouse (PPIC): < www.epa.gov/opptintr/library/libpic.htm >
EPIC U.S. DOE Pollution Prevention Information Clearinghouse: < epic.er.doe.gov/epic/ >
IRIS (Intergrated Risk Information System): < www.epa.gov/iris/ > [Provides access to a database containing summaries of health risk and regulatory information on more than 500 chemicals]
Small Business Ombudsman Hotline: 800-368-5888
Water
National Environmental Services Center (NESC): 800-624-8301 [Publications and techincal assistance related to drinking water and wastewater treatment technologies]
NESC National Small Flows Clearinghouse: < www.nesc.wvu.edu/nsfs/ >
NESC National Drinking Water Clearinghouse: < www.nesc.wvu.edu/ndwc/ >
Safe Drinking Water Hotline: 800-426-4791; < epa.gov/safewater >
Nonpoint Source (NPS) News/Notes: < www.epa.gov/owow/info/NewsNotes >
Wetlands Protection Hotline: 800-832-7828
Hazardous, Toxic, and Solid Waste
RCRA, CERCLA (Superfund), and EPCRA Assistance Hotline: 800-424-9346; < www.epa.gov/epaoswer/hotline/index.htm > [Answers to regulatory and technical questions on RCRA, CERCLA, and UST programs, and Emergency Planning and Community Right-to-Know Act (EPCRA); some documents available]
CERCLIS (Comprehensive Environmental Response, Compensation, and Liability Information System) Helpline: 703-908-2066, 202-260-0056 [Assistance for users of CERCLIS database]
Toxic Substances Control Act (TSCA) Assistance Information Service: 202-554-1404

Note: The information in this table is EPA sponsored unless otherwise indicated.

Source: U.S. EPA (1991) and other sources.

geologic settings are key to any ground-water investigation. These sources of information should be supplemented, if possible, by the original field *logs* of wells and test holes. These logs provide firsthand information on types and characteristics of rocks in the subsurface, their thickness, and areal extent. They also may describe drilling conditions that allow inference of relative permeability values, describe well construction details, and report water level measurements.

The Hydrologic Atlas (HA) and Water Resource Investigation (WRI) series of the U.S. Geological Survey are some of the best sources of hydrogeologic information. These maps are based

on the interpretation of all available geologic information from soil profiles, test wells, rock outcrops, observation wells, seismic surveys, and other means of subsurface observation. The location of aquifers on these maps is estimated by examining surficial geology, depth to bedrock, and depth to the water table. A hydrologic atlas contains information about ground-water availability, well locations, ground-water quality, surficial deposits influencing transmissivity, basin boundaries, flow characteristics of surface water, and other hydrologic factors. The U.S. Geological Survey has established a NAWDEX, which maintains a national database called WATSTORE, and U.S. EPA maintains a ground-water monitoring database called STORET (see [Table 5.13](#)). The USGS Water Resource Division District Office in each state can assist in obtaining data available from NAWDEX.

A water table or potentiometric surface map, if available, is another valuable source of hydrogeologic information (Section 7.2). Such maps may be available from the state water resource agency or geological survey. SCS-published soil surveys usually give summary data on monthly distribution, averages, and ranges of temperature and precipitation. The National Oceanic and Atmospheric Administration (NOAA) is the primary source for other climatological data, which may be required to evaluate recharge of unconfined aquifers. Hatch (1988/T5.13) provides a guide to types of data from NOAA's National Climate Data Center.

Geologic information is available from many sources. The U.S. Geological Survey and state geological surveys are the primary source for surficial and bedrock geologic maps. Important surface hydrologic features include drainage basins (watersheds), surface water bodies, wetlands, and flood zones. Wetlands can be identified on topographic maps; however, more detailed wetland maps may be available from the state wetlands regulatory agency or regional office of the U.S. Army Corps of Engineers. Flood mapping for every state has been prepared by the Federal Emergency Management Agency (FEMA). Two types of flood mapping are available: Flood Insurance Rate Maps (FIRMs) and Flood Boundary and Floodway Maps. These maps delineate the areas adjacent to surface waters that would be underwater in 100- and 500-year floods. Historic flood data may also be available from community and state libraries.

If published information sources are lacking or scarce, a review of well logs, both public and private, and test boring logs becomes the primary method for developing preliminary hydrogeologic interpretations for an area. Well records provide geological data (although the quality of descriptions prepared by water well drillers may be problematic). Records of well discharge and water level fluctuations may provide a basis for evaluating an aquifer's hydraulic conductivity, transmissivity, and storativity.

5.2.3 Air Photo Interpretation

Aerial photographs and *satellite imagery* are useful tools, both for office and field study. The latter should be examined first to detect trends of lineaments, which may indicate the presence of faults or joints. These may reflect zones of high permeability that exert a strong influence on fluid movement from the land surface or through the subsurface. Satellite imagery also can be used to indicate the presence of shallow ground water, where subtle tonal changes and differences in vegetation are caused by the higher moisture content. Rock types may also be evident.

Aerial photographs provide a relatively inexpensive way to directly observe natural and artificial features on the land surface. Much information can be obtained from stereopairs of black-and-white air photos, which provide a three-dimensional image of the surface when viewed with a stereoscope. Patterns of vegetation, variations in gray tones in soil and rock, drainage patterns, and linear features allow preliminary interpretations of geology, soils, and hydrogeology. All air photo interpretations should be field-checked and revised where "ground truthing" indicates features that were missed or incorrectly delineated. Section 6.2 provides additional information on remote sensing techniques.

Black-and-white air photos are available from various federal agencies for almost any location in the U.S. These are the cheapest type of air photo to obtain. The nearest county office of the Soil

Conservation Service or Agricultural Stabilization and Conservation Service (they will often be in the same building) is the best starting place to determine what is available. Many of these offices have air photo coverage that extends back to the 1930s. When photographs for multiple years are available, all should be examined, because significant features that are obscured in one set may be evident in another. Also, sequential examination of air photos taken at different times provides valuable information on changes in land use.

Air photos often reveal linear features, called fracture traces, that indicate zones of relatively higher permeability in the subsurface. Fracture-trace analysis using air photos can provide preliminary information on possible preferential movement of contaminants. Fetter (1980, pp. 406–411/T2.5) provides a good introduction to fracture-trace analysis. Parizek (1976)⁵ provides a good review of the North American literature on fracture-trace and lineament analysis.

5.3 DEVELOPING A SAMPLING AND MONITORING PLAN

Soil and ground-water sampling is conducted for a variety of reasons ranging from detection or assessment of the extent of a contaminant release to evaluation of trends in regional water quality. Initial sampling of soil and ground water should focus on locating the source and distribution of contaminants, if present, and characterizing geochemical variability. This information helps guide selection of locations for ongoing monitoring and identifies potential chemical problems that may affect selection and design of systems for soil and ground-water treatment. Soil-solute and ground-water sampling over a period provides information on the rate and magnitude of changes in ground-water quality.

Reliable sampling of the subsurface is inherently more difficult than either air or surface water sampling because of the inevitable disturbance caused by well drilling or pumping and the inaccessibility of the sampling zone. Consequently, monitoring well design and installation (Section 9.3) and sampling activities should be conducted so as to minimize disturbance of the subsurface geochemical and hydrogeologic conditions. A trained field team following a well-developed sampling protocol and communication between field and laboratory personnel are essential for coordinating sample handling and analysis.

5.3.1 Types of Monitoring

A complete sampling program for subsurface site characterization includes several types of monitoring, each with its own goal. The goal of *detection monitoring* is generally to determine the presence of contaminated conditions. For example, vadose zone monitoring (Section 9.1.1) allows early detection of subsurface contaminants before they enter the ground-water system. *Assessment monitoring* seeks to identify the extent and magnitude of contamination. For example, soil gas sampling allows relatively rapid initial delineation of areas contaminated by gasoline and other volatile nonaqueous phase liquids. If assessment monitoring results indicate a degree of contamination requiring remediation, *evaluation monitoring* is used to provide data necessary to design the remediation system. *Performance monitoring* is designed to evaluate the success of remediation efforts. Each stage of monitoring often requires the placement of additional monitoring wells and piezometers for water level measurements. Other types of monitoring include litigation monitoring in response to legal actions at contaminated sites and research monitoring aimed at specific scientific objectives.

⁵ Parizek, R.R. 1976. On the Nature and Significance of Fracture Traces and Lineaments in Carbonate and Other Terranes. In: Karst Hydrology and Water Resources, Vol. 1, V. Yevjevich, Ed., Water Resources Publications, Fort Collins, CO, pp. 3-1 to 3-62.

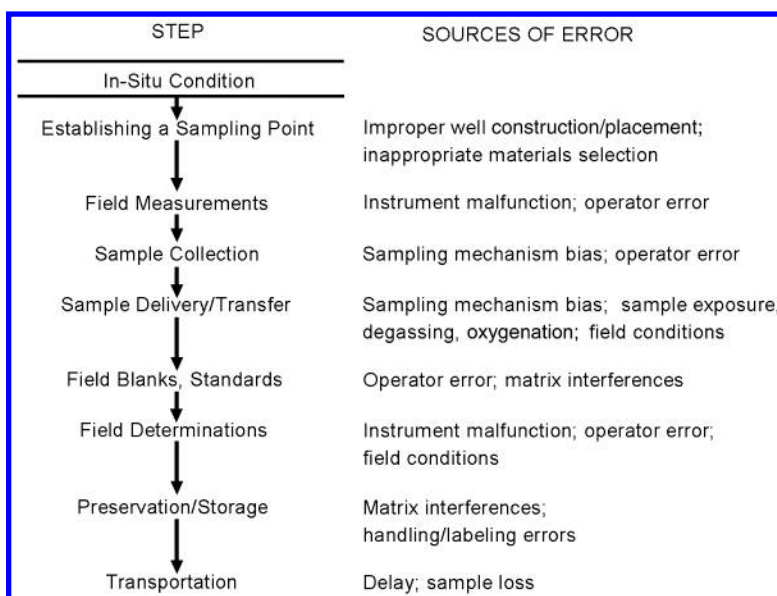


Figure 5.3 Steps in ground-water sampling and sources of error (Barcelona et al., 1985).

5.3.2 Sampling Protocol

A sampling protocol ensures the collection of data of known quality. Uncertainty, hydrogeologic variability, and quality assurance decision making need to be addressed from the initial design stage. Most initial effort and fiscal resources should be spent on characterizing basic site geology and hydrology, and sampling protocols should leave room for evolutionary development of the network design. For example, sampling experiments can be used to determine spatial correlation for solid samples. A large number of surface samples or split-spoon samples can be collected, but it may only be necessary to analyze a certain percentage (20 to 50%) to achieve adequate spatial coverage. If the initial sample groups indicate sufficient sampling resolution, the other samples need not be analyzed. If necessary, additional samples can be analyzed until geostatistical analysis indicates an adequate sampling intensity has been achieved.

Reliable protocols and the optimization of sampling procedures require particular attention to the effect of (1) sample location ([Section 5.3.3](#)), (2) sample frequency ([Section 5.3.5](#)), (3) sampling mechanism (Sections 9.4 and 9.5), (4) operator error, and (5) sample collection and handling procedures ([Section 5.3.6](#)) on both the sensitivity and reliability of chemical constituent monitoring results. Protocols should include documentation of all field activities, and deviations from the established protocol are necessary for a complete record of sampling activities, and useful if data collected for a particular purpose end up being used for other objectives.

Each step within the protocol affects the quality and completeness of the information being collected. Figure 5.3 lists the steps and corresponding sources of potential error in each phase of field collection of ground-water samples after a well has been properly purged of stagnant water. [Figure 5.4](#) identifies potential sources of error once a soil or ground-water sample reaches the laboratory. [Section 5.4](#) discusses sources of error further. Sections 9.4 and 9.5 address in more detail vadose zone and ground-water sampling methods, respectively.

Sampling protocols at contaminated sites or any site where there is a possibility for analyte cross-contamination should specify solutions and procedures for decontamination of portable sampling equipment after sampling at each location is completed. ASTM D5088 (Table A.14) provides guidance on decontamination procedures at nonradioactive waste sites. The appropriate state or federal agency should be consulted to identify required or preferred procedures. Mickam

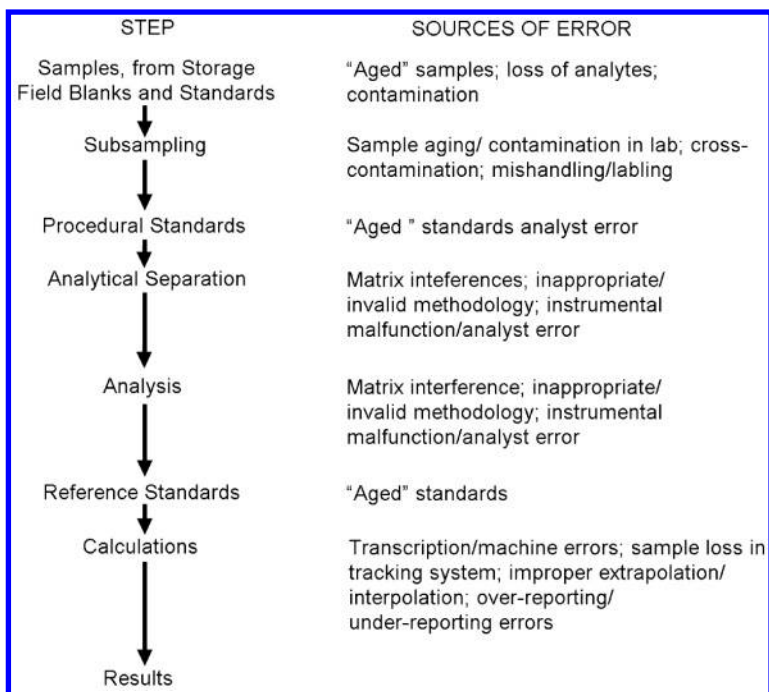


Figure 5.4 Steps in water sample analysis and sources of error (Barcelona et al., 1985).

et al. (1989)⁶ provide a good review of decontamination procedures in different EPA and state regulatory programs.

5.3.3 Sample Location

Sample location and frequency ([Section 5.3.5](#)) are among the most critical aspects of sampling because sample collection at the wrong location and time can give entirely erroneous results even when executed carefully. Initial selection of locations for sampling must be based on a good preliminary characterization of the geology and hydrogeology of the site, including good vertical and horizontal resolution of hydrogeologic conditions. This may require spending more of the available financial resources on hydrogeologic characterization than on chemical sampling and analyses. Additional sample locations should be added as understanding of the site evolves.

[Table 5.4](#) summarizes major types of sampling designs and when they should be used for characterizing subsurface geochemistry. In general, haphazard water quality or solid sampling is not an appropriate approach to designing sampling for subsurface geochemical characterization, even though professional judgment alone is probably the most frequently used method for siting ground-water monitoring wells. [Figure 5.5](#) illustrates some two-dimensional probability sampling designs for spatial characterization. The trends or patterns that commonly exist in subsurface contamination mean that simple random sampling will not give as accurate an estimate of population characteristics as stratified random and grid sampling designs.

Hydrogeologic characterization, initially using surface geophysical techniques followed by piezometers and preliminary well tests to estimate the distribution of hydrogeologic parameters, should come before the location and installation of monitor wells. Good vertical resolution is essential in sampling to characterize distribution of oxidized and reduced species, contaminants,

⁶ Mickam, J.T., R. Bellandi, and E.C. Tift, Jr. 1989. Equipment Decontamination Procedures for Ground Water and Vadose Zone Monitoring Programs: Status and Prospects. *Ground Water Monitoring Rev.* 9(2):100–121.

Table 5.4 Summary of Sampling Designs and Conditions for Their Use

Type of Sampling Design	Conditions When the Sampling Design Is Useful
Haphazard Sampling	
	A very homogeneous population over time and space is essential if unbiased estimates of population parameters are needed. This method of selection is <i>not</i> recommended due to difficulty in verifying this assumption.
Judgment Sampling	
	The target population should be clearly defined, homogeneous, and completely assessable so that sample selection bias is not a problem. Or specific environmental samples are selected for their unique value and interest rather than for making inferences to a wider population.
Probability Sampling	
Simple random	The simplest random sampling design. Other designs below will frequently give more accurate estimates of means if the population contains trends or patterns of contamination.
Stratified random	Useful when a heterogeneous population can be broken down into parts that are internally homogeneous.
Multistage Cluster	Needed when measurements are made on subsamples or aliquots of the field sample. Useful when population units cluster together (schools of fish, clumps of plants, etc.) and every unit in randomly selected cluster can be measured. Soil and ground-water contamination rarely, if ever, exhibit this characteristic.
Systematic	Usually the method of choice when estimating trends or patterns of contamination over space. Also useful for estimating the mean when trends and patterns in concentrations are not present or they are known <i>a priori</i> or when strictly random methods are impractical.
Double	Useful when there is a strong linear relationship between the variable of interest and a less expensive or more easily measured variable.
Search Sampling	
	Useful when historical information, site knowledge, or prior samples indicate where the object of the search may be found.

Source: Boulding and Barcelona (1991a), after Gilbert (1987).

and microbiota. Achieving this resolution requires more discrete well completions with short screens. In most cases, 5-ft to 1.5-m well screens should give adequate vertical resolution.

The spatial distribution of contamination is a major concern with sampling solids. The intensity and number of samples depend on the nonsampling variance, which is the variability of concentration that is unrelated to sampling procedures. Spatial structure determines the distance between samples that have essentially the same concentration, called the range of correlation, to avoid oversampling ([Section 5.6.2](#)).

There are two broad designs for soil sampling: (1) grids, in which samples are taken from a matrix of squares or quadrants at a site, and (2) transects, in which samples are taken at specified intervals along a line. Grids presume an aerial or dispersed source of some kind, and transects presume a preferential source. For example, Starks et al. (1986)⁷ established sampling transects where the length was proportional to the frequency with which wind blew in a particular direction to characterize metal contamination from a smelter near Palmerton, Pennsylvania. Flatman (1986/T5.14) describes use of geostatistics to determine sampling intensity. Grids can be used to estimate short-range correlation. Transects along the path of ground-water or contaminant movement provide the best way to look at long-range correlation. The combination of the two strategies coupled with the initial analysis of selected solid samples at alternate grid or transect locations can be quite effective.

⁷ Starks, T.H., K.W. Brown, and N.J. Fisher. 1986. Preliminary Monitoring Design for Metal Pollution in Palmerton, Pennsylvania. In: Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, Vol. 5, C.L. Perket, Ed., ASTM STP 925, American Society for Testing and Materials, Philadelphia, PA, pp. 57–66.

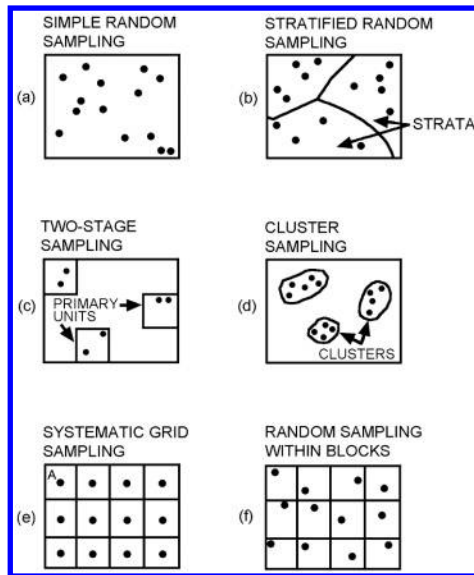


Figure 5.5 Some two-dimensional probability sampling designs for sampling over space (Boulding and Barcelona, 1991a, after Gilbert, 1987).

The combined strategy also can avoid the potential collection of redundant information. Using geostatistical analysis techniques of successive analytical subsets minimizes the number of samples actually analyzed. Transects could be both parallel and perpendicular to the axis of ground-water movement, along with some random samples from a grid, as shown in Figure 5.5f. Analysis of samples from four equally spaced locations on a transect or grid within the area of influence is a good starting point to estimate the distance of short-range correlation. For soils, at least 5% of sampling points should be duplicated to help determine the sampling variability so it can be analyzed with geostatistical techniques. At least 5% of the samples should be split as well.

Preliminary efforts that can help guide the location of initial wells for ground-water sampling include (1) surface geophysical techniques for mapping the extent of contaminant plumes, (2) soil gas sampling techniques, (3) drive-point ground-water samplers, and (4) selective sampling of drive-point piezometers for simple constituents such as pH, conductance, and possibly iron or dissolved oxygen concentrations.

Soil gas monitoring (Section 9.4.2), drive-point ground-water samplers such as Hydropunch® and BAT samplers (Section 9.5.2), and sequential sampling of drive-point piezometers probably give the best pictures of short-range variability in three dimensions. Sampling from monitoring wells usually gives some sort of integrated value depending on the relative width or thickness of the hydrogeologic formation of interest and the length of the screen. Disadvantages of soil gas concentrations include (1) lack of the ability to directly calibrate, because all values are relative and difficult to reproduce, (2) decontamination, and (3) short circuiting of air from the surface, which can distort results.

Locating both piezometers and monitoring wells spatially and vertically to ensure that they are monitoring the ground-water flow regime of concern is one of the most important components in a ground-water quality monitoring program. The placement and number of sampling points will depend on the complexity of the hydrologic setting, the diversity of source characteristics, and the degree of spatial and temporal detail needed to meet the program's goals. Piezometer and well placement should also be viewed as an evolutionary activity that may expand or contract as the needs of the program dictate.

In most monitoring situations, the goal is to determine the effect some surface or near-surface activity has had on nearby ground-water quality. Most dissolved constituents will descend vertically

Table 5.5 Chemical Constituents of Interest in Ground Water Monitoring

Type of Analyte	Where Done	Information Applications				Possible Source Impacts	Geochemical Evaluation of Data
		Water Quality	Drinking Water	Contamination			
Geochemical							
pH, Eh	F	X	X	X	X	X	
Conductivity	F	X	X	X	X	X	
Temperature	F	X	X	X	X	X	
Dissolved oxygen	F	X				X	
Alkalinity	F(FF)			X	X	X	
Ca ⁺² , Mg ⁺²	L(FF)					X	
Na ⁺ , K ⁺	L(FF)	X	X				
Cl ⁻ , SO ₄ ⁻² , PO ₄ ⁻²	F(FF)	X	X	X	X	X	
Silicate	L(FF)					X	
Water Quality							
Trace metals (Fe, Mn, Cr, Cd, Pb, Cu)	L(FF)	X	X	X	X	X	
NO ₃ ⁻ , NH ₄ ⁺	L(FF)	X	X	X	X	X	
F ⁻	L	X	X		X		
TOC	L	X	X	X	X		
TOX	L	X	X	X	X		
TDS	L(FF)	X	X	X	X	X	
Organic compounds	L	X	X	X	X		

Note: L = lab; F = field; FF = field filtered.

Source: Modified from Barcelona et al. (1989).

through the unsaturated zone beneath the area of activity and then, upon reaching the saturated zone, move horizontally in the direction of ground-water flow. Therefore, source monitoring points are normally completed downgradient in the first permeable water-bearing unit encountered. Upgradient points would be constructed to provide background or ambient water quality information.

In karst limestone terranes, ground-water monitoring wells are unlikely to intercept conduits that serve as the path for contaminant transport (Section 2.5.4). In this situation, monitoring of springs that have been identified as discharge points for the area of interest by dye tracing is the preferred method for monitoring ground-water quality. Section 7.5.4 discusses special considerations in hydrogeologic characterization of fractured rock and karst aquifers, and Section 8.4 addresses tracer tests in karst.

5.3.4 Sample Parameter/Analyte Selection

Soil Parameter Selection. Halocarbons, chlorinated hydrocarbon solvents (e.g., tetra- and trichloroethylene), and fuel constituents (e.g., toluene, benzene, ethyl benzene, and xylenes) are amenable to preliminary delineation by soil gas methods (see Table 9.7). Soil gas samples for carbon dioxide, methane, oxygen, and nitrogen can provide additional insights into subsurface chemistry, particularly microbiological activity. In addition to examining chemical constituents, solid samples should be analyzed for grain-size distribution and other parameters related to hydrologic properties (Section 7.4). Boulding (1994/T9.10) includes a checklist of more than 50 potential soil physical, hydrologic, and chemical parameters for evaluating contaminated sites.

Ground Water Parameter Selection. Table 5.5 and Table 5.6 identify chemical constituents of interest for various types of ground-water monitoring activities. In hazardous waste site investigations, regulations will generally specify the contaminants to be tested for. Focusing on priority

Table 5.6 Recommended Analytical Parameters for Detective Monitoring

Type of Parameter	Where Measured	Analytes	
		Required by Regulation	Suggested for Completeness
Well purging	F	pH, conductivity	Temperature Redox potential
Contamination indicators	F	pH, conductivity	
	L	TOC	
	L	TOX	
Water quality ^a	L	Cl ⁻ , Fe, Mn, Na ⁺ , SO ₄ ⁻²	Alkalinity (F) or acidity (F)
	L	Phenols	Ca ⁺² , Mg ⁺² , K ⁺ , NO ₃ ⁻ , PO ₄ ⁻² , NH ₄ ⁺ , silicate
Drinking water suitability ^b	L	As, Ba, Cd, Cr, F ⁻ , Pb, NO ₃ ⁻ , Se, Ag	
	L	Endrin, lindane, methoxychlor, toxaphene, 2,4-D, 2,4,5-TP (Silvex)	
	L	Radium, gross alpha/beta	
	L	Coliform bacteria	

Note: L = lab; F = field.

^a All parameters required to be determined quarterly for the first year of network operations (RCRA Part 265.92).

^b These parameters are excluded from the annual reporting requirements of RCRA after the first year.

Source: Barcelona et al. (1985).

pollutants alone, however, may not provide a complete geochemical picture of contamination. The source of contamination may involve a large number of individual contaminants that are not classified as hazardous. Also, determination of redox-sensitive constituents (dissolved oxygen and dissolved iron), pH, and conductance may provide valuable insight into subsurface contaminant geochemistry. Highly mineralized ground water, commonly encountered in formations being evaluated for deep-well injection of wastes, may require more complete analyses for natural inorganic and organic constituents.

Iron, an inexpensive constituent to determine analytically, can be used as an indicator of redox conditions and potential mobility for heavy metals. Dissolved gases are excellent indicators of redox conditions and microbial activity. For example, Leenheer and Malcolm (1973)⁸ analyzed for H₂, N₂, CH₄, CO₂, and H₂S in serial samples from a well through which a plume of deep-well-injected wastes passed. They used changes in the relative percentages of the different gases as indicators of changing microbial activity.

Battista and Connelly (1989)⁹ found that inorganic parameters such as chemical oxygen demand, specific conductance, chloride, alkalinity, and hardness were reasonably good indicators for predicting volatile organic compound (VOC) contamination from landfills. When the inorganic parameters were detected above background levels in monitoring wells, VOCs were also usually present. Of 49 ground-water samples at landfill sites in Wisconsin, VOCs and elevated inorganic parameters were detected at about the same frequency in 20 (41%), elevated inorganic parameters without VOCs were detected in 11 (22%), and VOCs without elevated inorganic parameters were detected in 3 (6%) wells. The remaining 15 wells in the study showed neither VOCs nor elevated inorganic parameters.

When organic contaminants are susceptible to biotransformation (Section 3.5.4), the list of analytes should include known daughter products. For example, trichloroethylene (TCE) yields a number of biotransformation products under anaerobic conditions (1,2-dichloroethene, 1,1-dichlo-

⁸ Leenheer, J.A. and R.L. Malcolm. 1973. Case History of Subsurface Waste Injection of an Industrial Organic Waste. In: Symp. on Underground Waste Management and Artificial Recharge, J. Braunstein, Ed., Intl. Assoc. of Hydrological Sci. Pub. No. 110, pp. 565–579.

⁹ Battista, J.R. and J.P. Connelly. 1989. VOC Contamination at Selected Wisconsin Landfills — Sampling Results and Policy Implications. WDNR PUBL-SW-09489. Wisconsin Department of Natural Resources, Madison, WI.

Table 5.7 Estimated Ranges of Sampling Frequency (in Months) to Maintain Information Loss at <10% for Selected Types of Chemical Parameters

Type of Parameter	Pristine Background Conditions	Contaminated	
		Upgradient	Downgradient
Water Quality			
Trace constituents (<1.0 mg/l)	2–7	1–2	2–10
Major constituents	2–7	2–38	2–10
Geochemical			
Trace constituents (<1.0 mg/l)	1–2	<2	1–5
Major constituents	1–2	7–14	1–5
Contaminant Indicator			
TOC	2	3	3
TOX	6–7	24	7
Conductivity	6–7	24	7
pH	2	2	1

Source: Boulding and Barcelona (1991c).

roethene, and vinyl chloride), which are also toxic. In fact, vinyl chloride is more toxic than TCE and is resistant to degradation under anaerobic conditions.

Calcium carbonate and iron/manganese concentrations are especially important parameters if remediation involves air stripping. Air-stripping towers are particularly susceptible to fouling by calcium carbonate and metal oxide precipitates.

5.3.5 Sampling Frequency, Type, and Size

Ground-Water Sampling Frequency. Table 5.7 shows estimated ranges of sampling frequency in months necessary to maintain information loss at less than 10% for selected types of chemical parameters. For many chemical constituents, quarterly sampling is adequate for characterizing short-term (i.e., monthly to 1 or 2 years) changes over time. For some reactive constituents such as iron and other redox-sensitive constituents, bimonthly sampling may be required.

With intermittent sources of contamination, it is especially important that the frequency of sampling not allow a contaminant to be missed. Barcelona et al. (1985/T9.10) describe a procedure for estimating sample frequency to detect contaminant plumes based on the type of plume (slug, intermittent, or continuous) and hydrogeologic parameters of gradient, hydraulic conductivity, effective porosity, and distance along the flow path. [Figure 5.6](#) shows a nomograph that can be used when these parameters are known. When the contaminant plume is a slug source or intermittent, sampling frequency should probably be more frequent to ensure that the plume is not missed. One advantage to the slow movement of ground water is that if there are questions about a sample, resampling a week later will yield roughly the same ground water.

Precise estimation of optimum sampling frequency is probably impractical for most investigations. For example, Bell and DeLong (1988)¹⁰ found that tetrachloroethylene at concentrations of 200 to 300 µg/l exhibited variations of a factor of 1 or 2 over the course of a year. Their work points out that data collection may be required for 4 years or more in order to estimate the optimal sampling frequency to determine seasonal variability. Therefore, it is important to select sampling frequency on the basis of an initial period of monitoring in the context of the duration of the program.

Soil Sample Type and Size. Soil sampling must take into account fractures in earth materials and the fact that the subsurface is heterogeneous (at scales ranging from centimeters to meters). If

¹⁰ Bell, H.F. and H.P. DeLong. 1988. Data Characteristics of Ground Water Monitoring's Catch 22. ACS Abstracts 28(2):20–24.

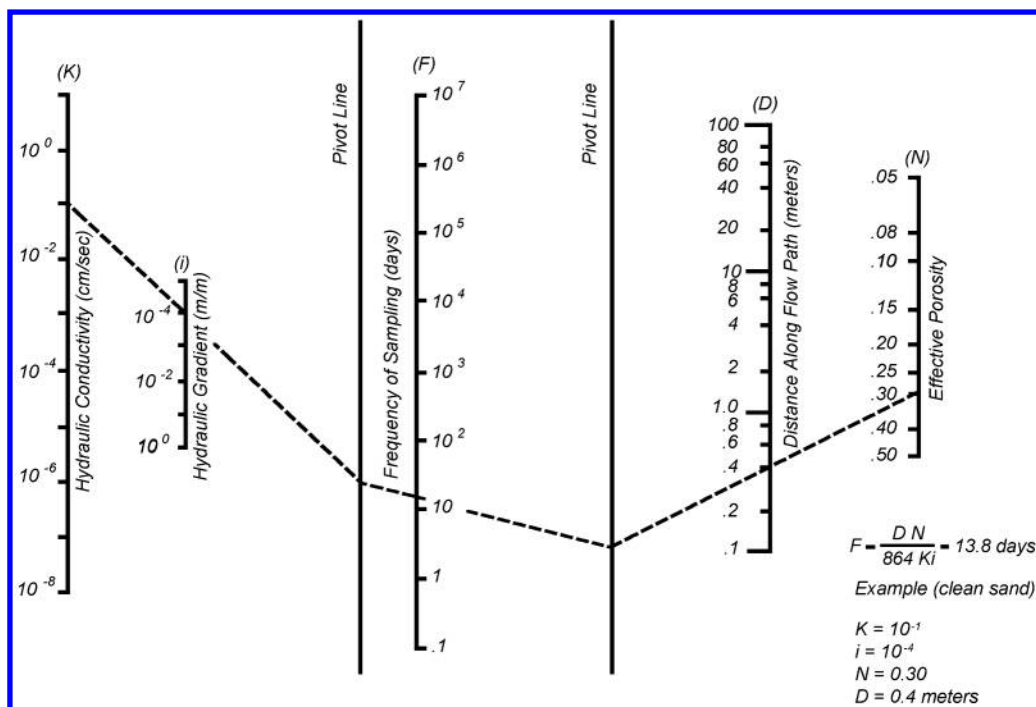


Figure 5.6 Sampling frequency nomograph (Barcelona et al., 1985).

the soil has obvious fractures and channels in the subsurface, sampling should sample both affected and apparently nonfractured areas for comparison. Soil sample quantities of less than 100 g tend to be unrepresentative even of the areas where the sample is taken. In the laboratory, the sample can be mixed and subsampled prior to analysis.

Compositing samples is often beneficial for soil investigations where constituents of interest are not volatile or redox sensitive. For example, Williams et al. (1989)¹¹ compared the results of one 500-g sample, twenty 25-g composite samples, and ten 50-g composite samples and found that a single 25-g composite sample was the most accurate and precise technique for determining radium concentrations in contaminated surface soil. Initial soil samples of 100 g are about the best size for such composite analyses.

5.3.6 Sample Collection and Handling

Container Selection. Sample containers should be free of contaminants prior to use and made of a material that will not alter the sample. Multiple sample containers will usually be required for each sampling point, with the number depending on the parameters to be analyzed. Each container must be clearly labeled, indicating the soil or well sample number and location. Table 5.8 lists the volume of sample required and the recommended container type for the analyses in a detective monitoring program. Table A.1 in Boulding (1994) provides similar information for soil sample containers.

Sample Collection.¹² Water samples should be collected when the major ion solution chemistry of the ground water being pumped has stabilized, as indicated by the pH, specific conductance,

¹¹ Williams, L.R., R.W. Leggett, M.L. Espegren, and C.A. Little. 1989. Optimization of Sampling for the Determination of Mean Radium-226 Concentration in Surface Soil. *Environmental Monitoring and Assessment* 12:83–96.

¹² The following discussion focuses on ground-water sample collection procedures. Appendix A in Boulding (1994/T9.10) is recommended for information on protocols for soil sample collection. Lewis et al. (1991/T9.10) address soil sampling for volatile constituents.

Table 5.8 Recommended Sample Handling and Preservation Procedures for a Detective Monitoring Program

Parameters (Type)	Volume Required (ml) 1 Sample ^a	Containers (Material)	Maximum Holding Period	Preservation Method
Well purging				
pH (grab)	50	T, S, P, G	None; field det.	<1 h ^b
Ω^{-1} (grab)	100	T, S, P, G	None; field det.	<1 h ^b
T (grab)	1000	T, S, P, G	None; field det.	None
Eh (grab)	1000	T, S, P, G	None; field det.	None
Contamination indicators				
pH, Ω^{-1} (grab)	As above	As above	As above	As above
TOC	40	G, T	Dark, 4°C	24 h ^d
TOX	500	G, T	Dark, 4°C	5 days
Water quality				
Dissolved gases (O ₂ , CH ₄ , CO ₂)	10-ml minimum	G, S	Dark, 4°C	<24 h
Alkalinity/acidity	100	T, G, P	4°C/none	<6 h ^b <24 h
	Filtered under pressure with appropriate media			
(Fe, Mn, Na ⁺ , K ⁺ , Ca ⁺² , Mg ⁺²)	All filtered 1000 ml ^f	T, P	Field acidified to pH <2 with HNO ₃	6 months ^c
(PO ₄ ⁻ , Cl ⁻ , silicate)	50	(T, P, G glass only)	4°C	24 h/7 days ^e ; 7 days
NO ₃ ⁻	100	T, P, G	4°C	24 h ^d
SO ₄ ⁻	50	T, P, G	4°C	7 days ^e
OH ₄ ⁺	400	T, P, G	4°C/H ₂ SO ₄ to pH <2	24 h/7 days
Phenols	500	T, G	4°C/H ₂ PO ₄ to pH <4	24 h
Drinking water suitability (As, Ba, Cd, Cr, Pb, Hg, Se, Ag)	Same as above for water quality cations (Fe, Mn, etc.) ^f	Same as above	Same as above	6 months
F ⁻	Same as chloride above	Same as above	Same as above	7 days
Remaining organic parameters	As for TOX/TOC, except where analytical method calls for acidification of sample			24 h

Note: T = Teflon; S = stainless steel; P = PVC (polyvinyl chloride), polypropylene, polyethylene; G = borosilicate glass.

^a It is assumed that at each site, for each sampling date, replicates, a field blank, and standards must be taken at volumes equal to those of the samples.

^b Temperature correction must be made for reliable reporting. Variations greater than $\pm 10\%$ may result from a longer holding period.

^c In the event that HNO₃ cannot be used because of shipping restrictions, the sample should be refrigerated to 4°C, shipped immediately, and acidified on receipt at the laboratory. Container should be rinsed with 1:1 HNO₃ and included with sample.

^d Twenty-eight-day holding time if samples are preserved (acidified).

^e Longer holding times in EPA (1986). See Appendix F for reference citation.

^f Filtration is *not* recommended for samples intended to indicate the mobile substance lead. See Puls and Barcelona (1989) (see Appendix F for reference citation) for more specific recommendations for filtration procedures involving samples for dissolved species.

Source: Boulding and Barcelona (1991c), after Scalf et al. (1981) and U.S. EPA (1986).

and temperature readings (Section 9.5.3). Samples should be collected as close as possible to the wellhead. A “tee” fitting placed ahead of an in-line device for measuring well-purging parameters makes this more convenient. During sampling, it is important to minimize the disturbance of fine particles that accumulate in the well. This can be achieved by careful placement of the sampling pump intake at the top of the screened interval, low pumping rates, and the avoidance of bailing

techniques, which disturb sediment accumulations at the bottom of the well. Well development may have to be repeated at periodic intervals to minimize the collection of turbid samples.

Aeration of ground-water samples should also be minimized. Wells located upgradient of a site (i.e., presumably uncontaminated) should usually be sampled first to minimize the potential for cross-contamination of sampling equipment from wells downgradient of the site.

The samples most sensitive to handling should be collected first. Figure 9.7 in Section 9.5 depicts a priority order for a generalized sample collection effort. In the figure, the samples for organic chemical constituent determinations are taken in order of decreasing sensitivity to handling; the inorganic chemical constituents, which may require filtration, are taken afterwards.

Samples collected for total organic carbon (TOC), total organic halogen (TOX), volatile compounds, field alkalinity, dissolved oxygen, and other analyses sensitive to pH and dissolved gases should not be filtered or transferred from one container to another, because of the potential for the loss of organic materials by volatilization or to the walls of the containers. To minimize volatilization, a flow-type sampling device (i.e., positive displacement pump) is generally best. Also, no headspace should exist in the sample containers. If solids content is high and may cause interference during organic determinations, the samples may be allowed to settle prior to analysis. Decanting this type of sample is preferable to filtration. If filtration is necessary to determine specific constituents (i.e., dissolved ferrous iron, other metals), pressure filtration should be performed in the field. Vacuum or gravity filtration of ground-water samples containing any parameters is not recommended.

Samples collected for dissolved inorganic chemical constituents, such as metals, alkalinity, and anionic species, are filtered in the field prior to acidifying for preservation. Samples can be filtered using a 0.45- μ glass or membrane filter (U.S. EPA, 1986/T9.10). The preferred filtering arrangement is an in-line filtration module that uses sampling pump pressure for its operation. These modules have tubing connectors on the inlet and outlet parts and range in diameter from 2.5 to 15 cm. Large-diameter filter holders, which can be rapidly disassembled for filter pad replacement, are the most convenient and efficient designs (Kennedy et al., 1976; Skougstad and Scarbo, 1968).¹³ Puls and Barcelona (1989)¹⁴ discuss further special considerations in handling samples for analysis of heavy metals.

Sample Preservation. The time between sampling and sample analysis can range from several hours to several weeks. Immediate sample preservation and storage can minimize changes in the chemical composition during this period, and can extend the time a sample can be held in the laboratory prior to analyses. Preservation methods usually involve pH adjustment, chemical addition, and refrigeration or freezing. Table 5.8, which lists sample volumes, also lists the preservation methods and acceptable holding times for the parameters in a detective monitoring program. Samples for dissolved metals analyses are not preserved until after filtration, which is normally performed in the field or in the laboratory as soon as possible after sampling.

Sample Transport. Samples should be chilled in the field immediately with ice and transported to the laboratory as soon as possible. The laboratory staff should be informed of the approximate time of arrival so that they can make all analytical determinations within storage periods. Sample packaging and method of transport must ensure that samples arrive at the laboratory on time and are neither lost nor damaged en route. Several commercial suppliers have sampling kits that include packing materials and freezer packs to keep the samples cold once they have been chilled to approximately 4°C (Kent and Payne, 1988).¹⁵ Special labels or distinctive storage vessels for samples preserved with acid in the field may be required to comply with shipping restrictions.

¹³ Kennedy, V.C., E.A. Jenne, and J.M. Burchard. 1976. Backflushing Filters for Field Processing of Water Samples Prior to Trace-Element Analysis. U.S. Geological Survey Water-Resources Investigations OFR 76-126.

Skougstad, M.W. and G.F. Scarbo, Jr. 1968. Water Sample Filtration Unit. Environmental Science and Technology 2(4):298–301.

¹⁴ Puls, R.W. and M.J. Barcelona. 1989. Ground Water Sampling for Metals Analyses. EPA Superfund Ground Water Issue Paper, EPA/540/4-89/001 (NTIS PB91-133249), 6 pp.

¹⁵ Kent, R.T. and K.E. Payne. 1988. Sampling Groundwater Monitoring Wells: Special Quality Assurance and Quality Control Considerations. In: Principles of Environmental Sampling, L.H. Keith (ed.), American Chemical Society, Washington, D.C., pp. 231–260.

Actual sample storage and treatment for samples that may contain hazardous constituents are documented using chain-of-custody procedures. The chain-of-custody record includes the date and times of sample collection, chain of possession, and time and date of receipt by the laboratory. After the laboratory receives the sample, the log is typically documented by the laboratory analytical chronology. The sampling team initiates the chain of custody in the field, and the manager in charge of the sampling program receives a copy of the form with the analytical report to verify sample storage and handling.

5.4 DATA MEASUREMENT AND RELIABILITY

The design of sampling and monitoring plans and the interpretation of data resulting from field investigations need to be based on a good understanding of (1) the characteristics of the system being observed (Section 5.4.1); (2) how representative the measurements are (Section 5.4.2); (3) the degree of measurement bias, precision, and accuracy (Section 5.4.3); and (4) sources contributing to error (Section 5.4.4).

5.4.1 Deterministic vs. Random Geochemical Data

Observation or measurement of physical phenomena can be broadly classified as either deterministic or nondeterministic. Deterministic data can be described by an explicit mathematical relationship. Nondeterministic or random data must be described in terms of probability statements and statistical averages rather than by the use of explicit equations. Figure 5.7 summarizes a classification scheme for deterministic and random data. The classification of physical data as

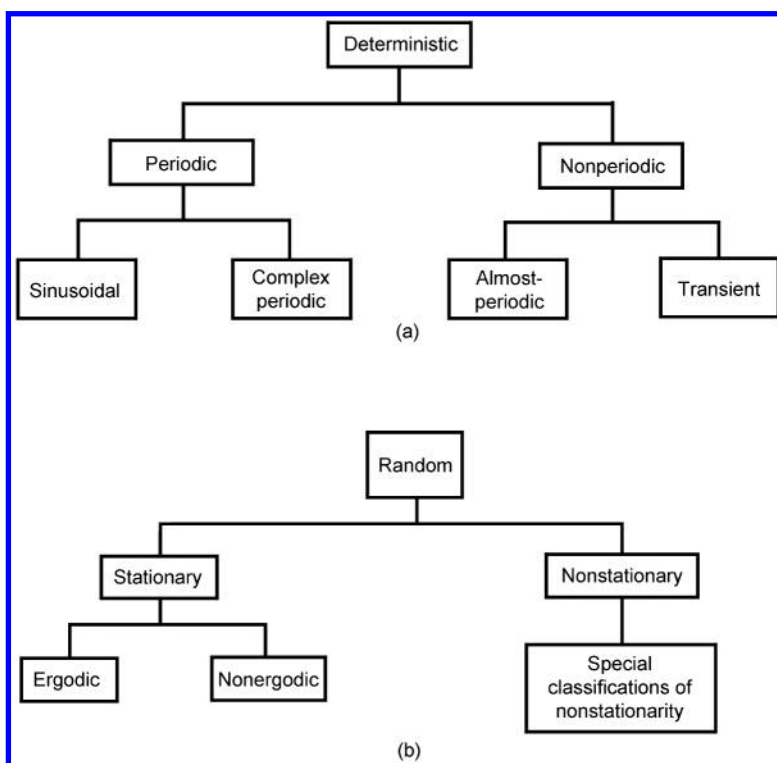


Figure 5.7 Classification of (a) deterministic and (b) random data (Boulding and Barcelona, 1991a, after Bendat and Piersol, 1986).

deterministic or nondeterministic is not always clear-cut in the real world. In fact, most geochemical data probably fall in a gray area between the two types. For example, the total dissolved solids (TDS) in an aquifer is a function of the chemical composition of the aquifer solids and residence time of the flowing ground water. Consequently, the distribution of sample values over space and time will not be completely random. On the other hand, the factors that determine the precise value of a given sample are sufficiently complex and variable that the distribution often cannot be predicted by an explicit mathematical equation.

The transient, nonperiodic data box in [Figure 5.7a](#) is a residual category that includes all data not included in the other boxes. This nonperiodic characteristic of geochemical data allows modeling of the distribution of geochemical species using thermodynamic principles. Essentially all geochemical modeling of the subsurface is done deterministically. The difficulty in accurately modeling the geochemistry of the subsurface can, however, be attributed to large random elements (see [Figure 5.7b](#)). Depending on the geochemical parameter, and the time frame of sampling, data may be stationary, where characteristics of the population being sampled do not vary over time, or nonstationary, where the random process varies with time. Typically, geochemical subsurface data involving contamination are nonstationary, but are not fully random (i.e., the value of one sample may show some correlation with the value of an adjacent sample). This creates special considerations in statistical analysis that are discussed in [Section 5.6](#). Subsurface physical parameters such as hydraulic conductivity, porosity, and soil particle-size distribution do not typically change with time, at least not on a timescale of human concern. These parameters, however, are not fully random.

5.4.2 Data Representativeness

In measuring environmental parameters, there is no “true” value, but rather a distribution of values. A representative unit or sample is one selected for measurement from a target population so that it, in combination with other representative samples, will give an accurate picture of the phenomena being studied (Gilbert, 1987/T5.14). Failure to take samples from locations and to use methods that yield samples that are representative of a site will result in the collection, at some expense, of analytical data that may be worthless. Representativeness determines whether accurate analysis of the samples will yield results that are close to actual conditions. Quality assurance/quality control systems in the laboratory or field may be useless if even greater emphasis is not placed on QA/QC in selecting locations and procedures for sampling ([Sections 5.3.3](#) and [5.3.6](#)).

Thorough site characterization of soils, hydrology, and geology, as described in subsequent chapters, is an essential prerequisite to geochemical sampling. This information provides the basis for developing sampling strategies that will provide some assurance that geochemical samples accurately reflect what is happening in the field. Sample representativeness is essentially knowledge based. For example, sampling locations selected by someone with a rudimentary understanding of sampling theory may yield less accurate results than locations chosen by an individual thoroughly grounded in this theory. At the same time, sampling locations selected without careful site characterization will yield less representative samples than locations selected with thorough site characterization, even with equally sophisticated application of sampling theory.

In contamination investigations, obtaining samples that can be considered representative for assessing one or more particular kinds of environmental exposure is a primary objective. This requires selecting not only the right place ([Section 5.3.3](#)), but the right type of sample ([Sections 5.3.4](#) and [5.3.5](#)).

5.4.3 Measurement Bias, Precision, and Accuracy

A measured value that is close to the estimate of the true average value is an unbiased or accurate value. This average or mean can only be estimated by a number of repeat determinations.

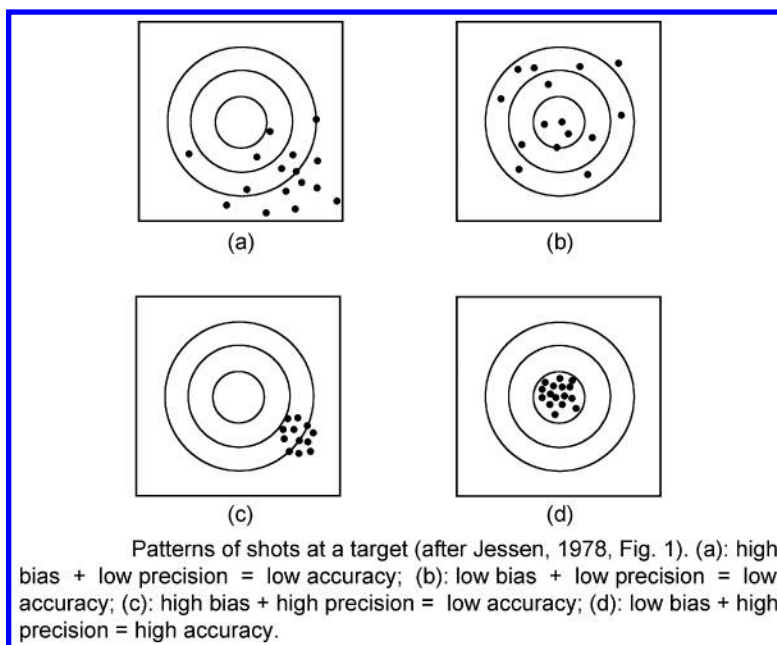


Figure 5.8 Shots on a target analogy for illustrating influence of bias and precision on accuracy (Boulding and Barcelona, 1991a, after Jessen, 1978).

Biased measurements will consistently under- or overestimate the true values in sampled population units. *Precision* is a measure of how closely individual measurements agree and is influenced principally by random measurement uncertainties. Both bias and precision influence *accuracy*, as illustrated in Figure 5.8. The center of each target in the figure represents the true value. Both low bias and high precision are required for high accuracy.

Accuracy is largely technologically based. In other words, accuracy can be improved by better drilling and monitoring well installation procedures and better sampling devices and procedures. Pennino (1988/T5.14) has suggested that “there is no such thing as a representative ground water sample” because of geochemical biases inherent in well installation, purging, and sample collection. However, a good understanding of both potential sources of error (see next section) and the way alternative sampling methods may bias results (Section 9.5) minimizes sample disturbance. The final evaluation of the results should be done with full consideration of the unavoidable disturbances involved in subsurface investigations.

5.4.4 Sources of Error

Random error results from slight differences in the execution of the same sampling procedure. Systematic error results from procedures that alter the properties of the sample. Random error is unavoidable, but must be evaluated to determine its effect on accuracy. For example, Figure 5.8b shows data with no systematic bias, but accuracy is low because random error is high. Systematic errors can be minimized by careful selection and consistent application of sampling techniques.

Figure 5.9 illustrates five possible sources of error in ground-water sampling: (1) site selection, (2) sampling, (3) measurement methods, (4) reference samples for calibration, and (5) data handling. Both random and systematic errors may be involved in each stage. Errors at each stage are cumulative, but are not of equal significance or magnitude. Total variance in geochemical data results from the combination of natural geochemical variability and the cumulative error. The percentage of variance attributable to natural variability may often be greater than either field or

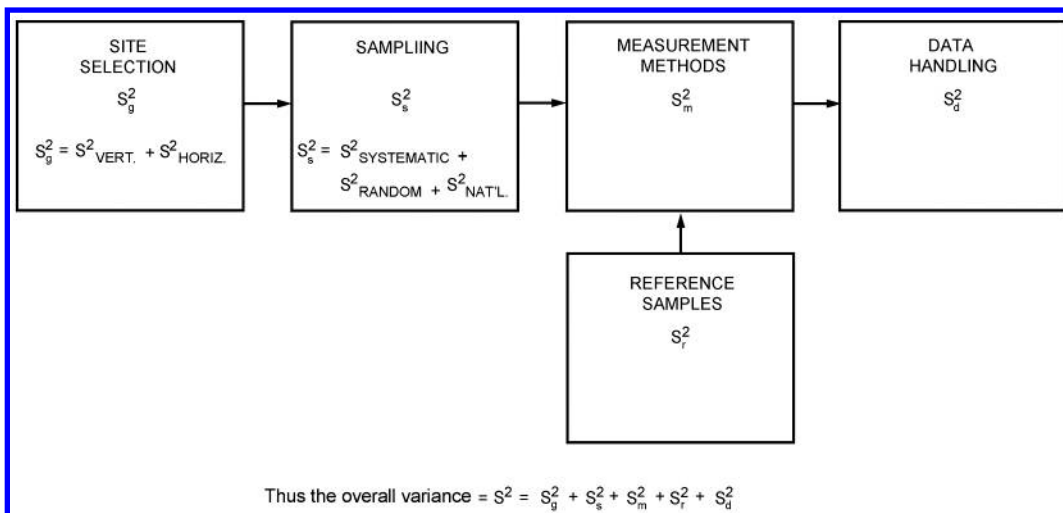


Figure 5.9 Sources of error involved in ground-water monitoring programs contributing to total variance (Barcelona et al., 1983).

laboratory error. Natural variance cannot be reduced; however, variance resulting from field and laboratory error can be reduced so that the actual variance closely approximates the natural variance.

Barcelona et al. (1989)¹⁶ developed estimates of the relative contribution of natural variability, field error, and laboratory error to total variance at three ground-water investigation sites in Illinois. For most chemical constituents, at the three sites, natural variability accounted for more than 90% of the variance. For most inorganic constituents where field and laboratory error could be estimated, field error contributed a larger percentage of total variance. The study also found that organic contaminant indicators (TOC and TOX) showed typically higher percentages of variance due to field and laboratory error than did the inorganic indicators.

Field Error. Figure 5.3 identifies specific possible sources of error at various steps in ground-water sampling. The largest sources of error are unrepresentative sample locations (hence the importance of hydrogeologic site characterization prior to geochemical sampling design) and disturbances caused by drilling and well construction. Sample collection is the next largest source of error. Major sources of systematic sampling error include (1) well construction and screen design preventing representative samples, and (2) improper purging. All of these large sources of systematic error are related to the hydrology of the site over which there is often little QA/QC.

Table 5.9 lists potential contributions of sampling methods and materials to error in ground-water chemical results. This table shows that well-purging procedures can result in large variations in pH, TOC, Fe(II), and VOCs. Table 5.9 shows well casing to be the next largest source of error, followed by sampling mechanisms and grouting/sealing. Poorly grouted or cemented wells can greatly alter the pH of water (as much as pH 12). Sampling tubing can result in errors in VOC measurement. Sections 9.5.3 (Purging) and 9.3 (Conventional Monitoring Well Installations) discuss selection criteria for minimizing errors from these sources.

Other possible sources of systematic error in sampling include (1) changing sampling procedures, (2) changing sampling personnel without a strictly defined sampling protocol, and (3) failure to document unavoidable deviations from the sampling protocols, such as no water in the well. Another source of water quality error is mixing from multiple aquifers. Mixing is most common with public water supply wells that penetrate several hydrologically unconnected aquifers. Improper sealing of ground-water monitor wells also may bias results by mixing water from distinct subsurface formations.

¹⁶ Barcelona, M.J., D.P. Lettenmaier, and M.R. Schock. 1989. Network Design Factors for Assessing Temporal Variability in Ground-Water Quality. *Environmental Monitoring and Assessment* 12:149–179.

Table 5.9 Potential Contributions of Sampling Methods and Materials to Error^a in Ground Water Chemical Results

Sampling Method/Material	pH	Chemical Parameter		
		TOC (mg C/l)	Fe(II) (mg/l)	VOC (µg/l)
Range of concentration	5–9	0.5–25	0.01–10	0.15–8000
Drilling muds	—	+, 300%	—	—
Grouts, seals	+, 4–5 units (cement)	—	—, ^b 500% cement	—
Well purging	±, 0.1–5 units	±, 500%	—, ^b 1000%	±, 10–1000% ^c
Well casing	—	±, 200%	+, 1000% iron, galvanized steel	±, 200% ^c
Sampling mechanism	Gas lift +, 0.1–3 units	Bailer +, 150%	Gas lift —, ^b 500%	Suction —, ^b 1–15% ^d
Sampling tubing	—	—	—	–10 to 75% ^d
References ^e	1, 5, 7	1, 4	1, 2, 5, 7	1, 3, 6

^a Bias values exceeding ±100% denoted as gross errors (+ or –); other values expressed as a percent of reported mean.

^b No data available on the type and extent of error for this parameter.

^c Concentration range of 0.5–15 µg/l (from Barcelona and Helfrich, 1984).

^d Concentration range of 80 to 8000 µg/l (from Barcelona et al., 1984; Ho, 1983).

^e References (see Appendix F for citations): 1 = Barcelona and Helfrich (1984); 2 = Barcelona et al. (1983); 3 = Barcelona et al. (1984); 4 = Barcelona et al. (1988); 5 = Gibb et al. (1981); 6 = Ho (1983); 7 = Schuller et al. (1981).

Analytical Error. Figure 5.4 identifies possible sources of error during water sample analysis. Analysis, including measurement methods and reference samples, is typically subject to the most stringent QA/QC procedures, and consequently, analytical errors tend to be relatively minor components of total error. Failure to analyze blanks, standards, and samples by exactly the same procedures may result in either a biased blank correction or a biased calibration (Kirchmer, 1983/T5.14). Porter (1986/T5.14) examined in detail the sources of random analytical error for measurement near the limit of detection and how to incorporate this observation error into data analysis procedures.

Einarson and Pei (1988)¹⁷ and Rice et al. (1988),¹⁸ in separate studies of laboratory performance, concluded that the reliability of laboratory analyses should not be taken for granted. Both studies also concluded that the cost of analysis did not necessarily correlate with analytical accuracy. The most expensive of the 10 laboratories evaluated by Einarson and Pei tied for the worst ranking, while the 4 least expensive laboratories included the top-ranked and other bottom-ranked laboratory. Both studies describe criteria and procedures for choosing laboratories that will provide good analytical results. Section 5.5 discusses analytical and QA/QC concepts further.

Data Handling Error. There is probably no large body of scientific records free from human or machine errors. Faulty recording of observations in field or laboratory notebooks and incorrect coding for computer analysis are examples of data handling errors. Misrecorded values that are much larger or smaller than the range of the actual population are called outliers and may distort the results of statistical analysis. Statistical techniques are available for analyzing such data sets (Gilbert, 1987/T5.14), but prevention of data handling error is always better than a cure. Censoring of analytical measurements below the limit of detection (Section 5.5.2) is another serious error introduced by data handling.

Webster (1977/T5.14) suggests some of the following methods to reduce data handling errors: (1) write neatly, forming characters well; (2) distinguish ambiguous digits and letters by a firm convention; (3) restrict the digit 0 to mean zero and use other notations for “missing” or “inappli-

¹⁷ Einarson, J.H. and P.C. Pei. 1988. A Comparison of Laboratory Performances. *Environmental Science and Technology* 22:1121–1125.

¹⁸ Rice, G., J. Brinkman, and D. Muller. 1988. Reliability of Chemical Analyses of Water Samples: The Experience of the UMTRA Project. *Ground Water Monitoring Review* 8(3):71–75.

cable”; (4) eliminate or minimize transcription of field notes; (5) record data on forms designed for the purpose of the investigation with clear headings and ample space; and (6) double-check any transcribed data against the original.

5.5 ANALYTICAL AND QA/QC CONCEPTS

Quality assurance and quality control are accomplished by (1) selecting the best methods for the program purpose, (2) clearly defining protocols or procedures to be followed, and (3) carefully documenting adherence or departures from the protocols. Both field sampling and laboratory analyses require protocols for good QA/QC. Campbell and Mabey (1985)¹⁹ have summarized key elements of data evaluation systems applicable to both field and laboratory measurements. [Table 5.13](#) identifies major reports and papers on QA/QC for environmental investigations.

5.5.1 Instrumentation and Analytical Methods

A bewildering array of methods are available for analyzing geochemical constituents. Most methods used for geochemical analysis involve either emission or adsorption of radiation (Table 9.9, Section 9.6.3). The fine points of instrumentation and analysis are the province of the analytical chemist, but the field scientist can benefit from a general understanding. Section 9.6 provides additional information of field screening and analytical methods. Analytical techniques for specific constituents of geochemical interest may be specified by regulation or, if not so specified, determined by the instrumentation that is most readily available. Table 9.10 identifies major references describing chemical analytical techniques.

5.5.2 Limit of Detection

Ground-water detection monitoring commonly involves measurement of contaminants that are either at or below the detection limit of analytical procedures. The statistical concept of detection limit includes accurately reporting and analyzing data, including measurement near or below the detection limit (McNichols and Davis, 1988/T5.14).

[Figure 5.10](#) and [Table 5.10](#) illustrate the definitions of limit of detection and regions of analyte measurement recommended by the Subcommittee on Environmental Analytical Chemistry of the American Chemical Society’s (ACS) Committee on Environmental Improvement (1980/T5.14). The zero analyte signal for measuring the limit of detection comes from the field blank (see below). If the actual field blank measurement gives a positive signal, this means that analytical measurements on other samples with a lower signal will be recorded as a negative concentration. For example, a low concentration standard (typically 1 part per billion (ppb) for organic constituents) is made in the laboratory for the contaminant of interest. The standard deviation for analytical measurement of the 1-ppb standard is commonly plus or minus 100%, or 1 µg/l. The detection limit for a contaminated sample is defined as 3 standard deviations (3 µg/l) above the mean for the standard, or 6 standard deviations above the zero point defined by the field blank (see [Figure 5.10](#)). The limit of detection should be defined every day of analysis. The detection limit is probably the most important kind of laboratory quality assurance data and should be reported with the analytical results for each constituent.

Table 5.10 lists the regions of analyte measurement. Following the above example, signals below 3 standard deviations are considered below the limit of detection. The region of detection is between 3 and 10 standard deviations (5 standard deviations by some rules) and is where the constituent can

¹⁹ Campbell, J.A. and W.R. Mabey. 1985. A Systematic Approach for Evaluating the Quality of Ground Water Monitoring Data. *Ground Water Monitoring Rev.* 5(4):58–62.

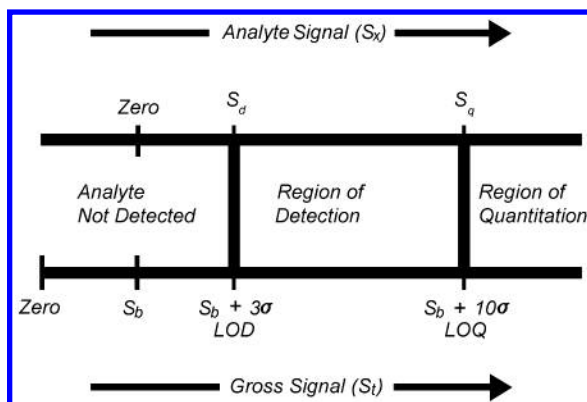


Figure 5.10 The ACS recommended definition of limit of detection (Boulding and Barcelona, 1991a, after ACS Comm. on Environmental Improvements, 1980).

Table 5.10 Regions of Analyte Measurement

Analyte Signal (standard deviations in $\mu\text{g/l}$)	Recommended Inference
<3	Analyte not detected
3–10	Region of detection
>10	Region of quantitation

Source: Boulding and Barcelona (1991a), after ACS Committee on Environmental Improvement (1980).

be said to be present but the precise concentration cannot be stated with certainty. Analyte signals above the limit of quantification (plus 10 standard deviations) can be interpreted quantitatively.

The above-described definition reaffirms the model for limit of detection calculations adopted by the International Union of Pure and Applied Chemistry (IUPAC) in 1975 (IUPAC, 1978/T5.14). However, considerable confusion still surrounds the definition of the limit of detection. This is because (1) acceptance of the above definition by the general analytical community has been slow, and (2) different statistical approaches to calculating limits of detection for constituents can easily vary by an order of magnitude (Long and Winefordner, 1983/T5.14). This is particularly true for chemical constituents at the parts per billion level.

The limit of detection is both a site- (as a result of the field blank) and instrument-/operator-specific value. Consequently, the precision and accuracy for low standards must be reported on the analytical report forms. The instrument manufacturer's definition of detection is based normally on carefully controlled conditions (e.g., distilled water solutions) that may not be achievable in routine analyses of complex samples. Consequently, actual limits of detection in contaminated ground water are often higher.

Data Censoring. A major problem with failure to understand the statistical nature of the limit of detection is negative censoring of data. *Negative censoring* involves reporting analyte concentrations that are below the limit of detection as zero, less than values, or not detected. Since 1983 the American Society for Testing and Materials has recommended that data should not be routinely censored by laboratories (ASTM D4210/Table A.14). Nevertheless, censoring of water quality analytical data remains a problem (Porter et al., 1988/T5.14). [Section 5.5.1](#) examines this issue further.

Laboratories should be asked to provide uncensored data on all water samples with measurements near or below the limit of detection. Measurement data should not be discarded unless the lack of statistical control in the measurement process is clearly demonstrated. The general public, and even the uninformed scientist, may find the concept of a negative concentration difficult to understand, so it is prudent to report less than zero values as “trace” when presenting data in tables

Table 5.11 Effects of Censoring Analyte Signals at and below the Limit of Detection

Sample	Heavily Censored	Negatively Censored	Uncensored
1	<3	2	2
2	<3	0	-2
3	<3	0	-1
4	4	4	4
5	3	3	3
6	<3	0	-3
7	<3	1	1
8	<3	0	-1
9	<3	0	0
10	<3	2	2
Mean	3.5	1.2	-0.5
95% confidence interval	0.14–2.26	1.13	-2.13

Source: ASTM D4210/TA.14.

that present data in the main body of a report. Remediation decisions, however, should be based on concentrations at or above the limit of quantification, not the limit of detection.

Analysis of Censored Data. Table 5.11 illustrates the effect of two types of censoring of analytical results near and below the limit of detection. Data reported as less than the limit of detection are heavily censored and yield an average concentration of 3.5 µg/l, since only two values are quantified. In Table 5.11 negative censoring (see definition above) yields an average of 1.2 µg/l. The uncensored data average 0.5 µg/l. The averages of the heavily and negatively censored data would appear to indicate contamination, but the 95% confidence interval for the uncensored data is at best equivocal. Gilliom et al. (1984/T5.14) found that any censoring of trace-level water quality data, even when the censored data were highly unreliable, reduced the ability to detect trends in the data. Unfortunately, censored data continue to be routinely reported by laboratories. [Table 5.14](#) identifies a number of references that discuss statistical techniques for analyzing censored data.

5.5.3 Types of QA/QC Samples

Field scientists tend to consider QA/QC requirements and procedures to be primarily the responsibility of the laboratory. However, QA/QC procedures are equally, if not more, important in the field. Field personnel also should be familiar with the different types of samples that may be taken, and their importance for interpreting the analytical results. Field sampling programs typically involve collection of additional sample volumes from a number of wells (typically 10 to 20%) for laboratory quality control for matrix spikes and replicate analyses. For specific programs, it may be appropriate to prepare field standards and field spiked samples, and to collect blind control samples to provide an independent check on the performance of the analytical laboratory.

Major types of field and QA/QC samples include the following:

- A *trip blank* is a sample bottle filled with laboratory analyte-free water that travels to the site with the empty sample bottles and is returned to the laboratory with the samples. The trip blanks are not opened in the field. They provide a method of monitoring bottle preparation, blank water quality, and sample handling. Contaminated trip blanks may indicate poor-quality laboratory water or inadequate bottle cleaning.
- A *field blank* is a sample of distilled or deionized water taken from the laboratory out into the field, poured into a sampling vial at the site, closed, and returned as if it were a sample. The level of contamination of the field blank is the zero analyte signal for determining the limit of detection.
- A *rinse or cleaning blank* is a sample of the final rinse of a sampling mechanism before it is put in a new well. This type of sample is used to evaluate whether a sample may have been contaminated from material taken in the previous sample.

- *Field samples* are those samples that are taken in the field as representative of conditions at the site and analyzed in the laboratory for constituents of interest. If sampling points or locations are unrepresentative, or biased sampling procedures are used, no amount of care in QA/QC in subsequent stages will salvage an accurate picture of actual field conditions.
- *Duplicate samples* are collected and not analyzed unless it is later determined that they contain additional useful information. Soil samples are commonly duplicated.
- *Replicate samples* are subsamples of the same sample that are labeled separately to estimate the precision of laboratory analytical results.
- *Split samples* are field samples that are split between two storage vessels or cut in half in the field. One subsample may be analyzed by one laboratory and the other subsample may be archived or given to another laboratory.
- *Spiked samples* are field samples that may be split with one aliquot receiving a spike volume of a reference standard to estimate the recovery of the analyte in the laboratory. Spiked samples allow estimates of accuracy and detect possible matrix interference problems.
- *Laboratory blanks* are similar to field blanks except that the distilled deionized water used in the laboratory at the time each batch of samples is received is analyzed in the same manner as other samples. This type of sampling may detect contamination that occurs in the laboratory.
- *Standard reference samples* have been analyzed previously by outside laboratories. These samples are available from the National Institute of Standards and Technology or the EPA to detect either instrument calibration error or the use of inappropriate laboratory analytical methods (Keith et al., 1983).²⁰

5.6 STATISTICAL TECHNIQUES

5.6.1 Statistical Approaches to Geochemical Variability

Virtually all soil sampling and most ground-water sampling that have been done at a high enough level of resolution have shown that chemical constituent concentrations are neither normally distributed nor independent (i.e., noncorrelated). This creates special challenges for statistical analysis of geochemical sampling data because many of the traditional statistical techniques for analyzing sample data, such as linear regression and t-testing, assume that the population sampled has the symmetric, bell-shaped Gaussian (normal) distribution. Linear regression is probably the most frequently misused statistical technique in this context (Mann, 1987; Kite, 1989).²¹

The first step in analyzing geochemical data is to determine whether they are normally distributed. If they are, traditional techniques described in standard textbooks on statistics can be used. If not, one or more of the following methods must be used: (1) *data transformations* such as logarithmic conversions to create data sets that are normally distributed, and hence amenable for analysis by conventional methods (Wilson et al. (1990)²² discuss how to evaluate bias that may be introduced by this manipulation); (2) *nonparametric* or distribution-free statistical techniques that do not require independent data observations; and (3) *geostatistical* techniques that facilitate differentiation of correlated and noncorrelated data sets and interpolation of values between sample points. The technique of “fuzzy” linear regression may be useful in hydrologic situations where the relationship between variables is imprecise, data are inaccurate, or sample sizes are insufficient (Bardossy et al., 1990).²³ Subsurface contamination investigations typically involve measurements

²⁰ Keith, S.J., M.T. Frank, G. McCarty, and G. Massman. 1983. Dealing with the Problem of Obtaining Accurate Ground-Water Quality Analytical Results. In: Proceedings of the 3rd National Symposium on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 272–283.

²¹ Kite, G. 1989. Some Statistical Observations. *Water Resources Bulletin* 25(3):483–490. See also discussion by Kirby et al. (1990), and reply by Kite in *Water Resources Bulletin* 26(4):693–698. Mann, J.C. 1987. Misuses of Linear Regression in Earth Sciences. In: *Use and Abuse of Statistical Methods in the Earth Sciences*, W.B. Size (ed.), Oxford University Press, New York, pp. 74–106.

²² Wilson, B.G., B.J. Adams, and B.W. Karney. 1990. Bias in Log-Transformed Frequency Distributions. *Journal of Hydrology* 118:19–37.

²³ Bardossy, A., I. Bogardi, and L. Duckstein. 1990. Fuzzy Regression in Hydrology. *Journal of Hydrology* 26(7):1497–1508.

of concentration changes in geochemical parameters over time. Consequently, statistical techniques designed specifically for analysis of trends in time-series data are important (Harris et al., 1987; Montgomery et al., 1987/T5.14).

Alhajjar et al. (1990)²⁴ describe use of the *median-polish* statistical methods of exploratory data analysis developed by Tukey (1977/T5.14) for analyzing highly variable geochemical data collected during a study of chemical pollution from septic systems. This technique is especially well suited for analyzing data in two-way tables (multiple rows and columns) in which each data value is related simultaneously to two factors.

5.6.2 Geostatistics

Geostatistical techniques such as the use of correlograms, semivariograms, and kriging have gained increasing popularity in evaluating spatially distributed hydrologic and geochemical data in the last 10 years. Using empirical gold ore evaluation techniques developed by D.C. Krige in South Africa (hence the term *kriging*), the French mathematician G. Matheron developed the theory of regionalized variables in the late 1960s (Matheron, 1971/T5.14). This general theory of sampling and estimating spatially dependent (autocorrelated) variables is well suited to analysis of hydrologic and geochemical parameters, which tend to be nonrandom in the classical Gaussian statistical sense.

Geostatistical techniques have three main applications for characterization of subsurface variability: (1) they can assist in reducing spatial sampling intensity, and hence reduce sampling and analytical costs; (2) they can be used to differentiate sample data that are autocorrelated or noncorrelated, elucidating trends for selecting the appropriate statistical analysis of sampling analytical results; and (3) they can be used to interpolate values at locations where measurements have not been made. The last application is done by *kriging*, a weighted moving-averaging technique that usually provides the most accurate way of contouring data on physical and geochemical parameters. An advantage of kriging is that a standard deviation map can be readily created from kriged contour data, which provides a good indication of the reliability of contours. However, when the variogram (see below) is not well defined and expected values of the mean and variance are not constant over the area of interest, other interpolation techniques, such as inverse distance interpolation methods, may produce superior contouring results compared to kriging.²⁵

One of the first steps in geostatistical analysis is to calculate the nonsampling variance (γ) of samples at different distance spacings. γ is a statistical measure of the difference between sample values. For example, if samples were taken from a 50-m grid, γ would be calculated for the samples spaced at 50, 100, 150, 200 m, and so on. Next, a semivariogram is plotted on an XY plot, where X is distance and Y is the nonsampling variance. Figure 5.11 shows an “ideal” semivariogram. Samples within a certain range of influence, also called the range of correlation (distance a in Figure 5.11), show an approximately linear correlation (are autocorrelated). At some spacing distance, if there is no trend in the data, a sill (c on Figure 5.11) marks a plateau that limits the range of correlation. The nonsampling variance between samples will equal c as long as the distance is greater than a .

From a sampling perspective, samples spaced closer than distance a in Figure 5.11 will yield redundant, correlated data, which results in both unnecessary expense and complications in statistical analysis. The minimum distance at which samples are independent (distance a in Figure 5.11) is the optimum sampling distance.

Figure 5.12 shows a semivariogram of lead values in soil sampled by Flatman (1986/T5.14) on a systematic 750-ft grid. The diagram shows that samples for lead that are closer to each other

²⁴ Alhajjar, B.J., G. Chesters, and J.M. Harkin. 1990. Indicators of Chemical Pollution from Septic Systems. *Ground Water* 28(4):559–568.

²⁵ Weber, D. and E. Englund. 1992. Evaluation and Comparison of Spatial Interpolators. *Mathematical Geology* 24(4):381–391.

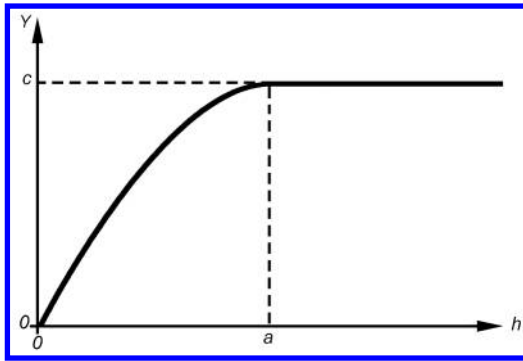


Figure 5.11 The “ideal” shape for a semivariogram–spherical model (Boulding and Barcelona, 1991a, after Clark, 1979).

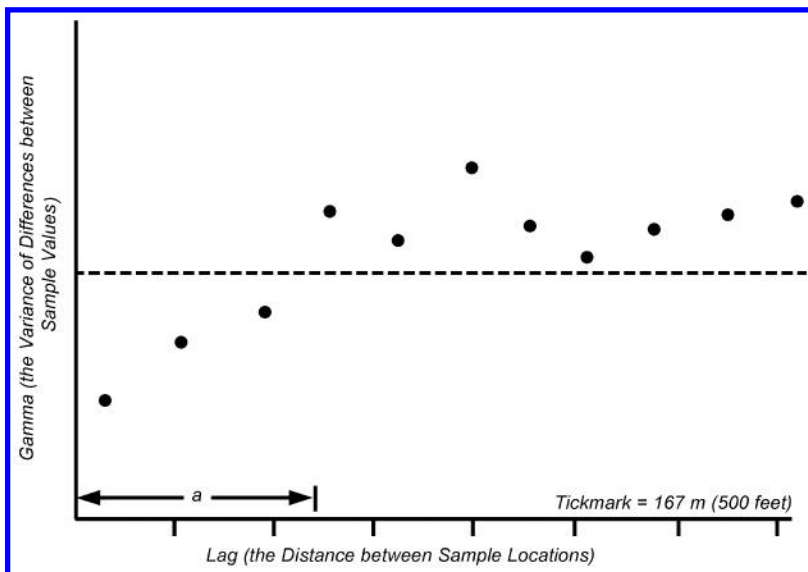


Figure 5.12 A semivariogram of lead samples taken systematically on a 230-m (750-ft) grid (Boulding and Barcelona, 1991a, after Flatman, 1986).

than about 1200 ft are correlated. In other words, the same information could be obtained by cutting the number of samples almost in half.

Semivariograms may exhibit correlation structures other than the one shown in Figure 5.12, and correct interpretation requires an understanding of the various models that are available for describing semivariogram plots. When data are not normally distributed, such as when a spatial trend is present, estimating the correlation structure is difficult. In these cases, some of the techniques for transforming lognormal data for conventional statistical analysis may be useful.

5.7 GUIDE TO MAJOR REFERENCES

[Table 5.12](#) provides a listing of major conferences and symposia series that address a variety of aspects of soil and ground-water contamination and investigation techniques. Selected NWWA/NGWA conference proceedings are published by the National Ground Water Association (formerly the National Water Well Association): 601 Dempsey Road, Westerville, OH 43081;

800-551-7379. In the late 1990s the Hazardous Materials Control Research Institute (HMCRI) stopped sponsoring and publishing its conference series that contain many papers relevant to contaminant investigations. There is no single library that has a complete collection of the HMCRI conference proceedings.

[Table 5.13](#) provides an index of major references on existing sources of environmental information, environmental data management, and quality assurance/quality control. [Table 5.14](#) provides an index of major references on basic and environmental statistics and sampling design.

Table 5.12 Conferences and Symposia with Papers Relevant to Subsurface Characterization and Monitorings^a

Sponsor	Year	Title
EPA/NWWA	1971	1st National Ground Water Quality Symposium (EPA-16060 GRB, NTIS PB214-614)
	1974	2nd (EPA-68-03-0367, NTIS PB257-312)
	1977	3rd (EPA/600/9-77/014, NTIS PB272-908)
	1979	4th (EPA/600/9-79/029, NTIS PB80-103476)
	1980	5th
	1983	6th (State, County, Regional, and Municipal Jurisdictions of Ground Water Protection)
	1984	7th (Innovative Means of Dealing with Potential Sources of Ground Water Contamination)
NWWA	1986	8th (Anatomy of Superfund)
	1981	1st National Ground Water Quality Monitoring Symposium and Exposition
	1982	2nd National Symposium on Aquifer Restoration and Ground Water Monitoring
	1983	3rd
	1984	4th
	1985	5th
	1986	6th
	1987	1st National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring, and Geophysical Methods
	1988	2nd
	1989	3rd
NGWA	1990	4th GWM 2
	1991	5th GWM 5
	1992	6th GWM 11
	1993	7th GWM 15
	1994	8th GWM 18
	1995	9th
	1996	10th
	1997	11th
NWWA/API	1984	[1st] Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration
	1985	[2nd]
	1986	[3rd]
	1987	[4th]
	1988	[5th]
	1989	[6th]
	1990	[7th] GWM 4
	1991	[8th] GWM 8
NGWA/API	1992	[9th] GWM 14
	1993	[10th] GWM 17
	1994	[11th]
	1995	[12th]
	1996	[13th]
	1997	[14th]
	1998	[15th]
	1999	16th]
	2000	[17th]
	2001	[18th]
	2002	[19th]
NWWA Eastern Regional Conferences		
NWWA/AGWSE	1984	[1st] Eastern Regional Ground Water Conference
	1985	[2nd]
	1986	3rd Annual Eastern Regional Ground Water Conference
	1987	4th
	1988	[5th] Focus Conference on Eastern Regional Ground Water Issues
	1989	[6th]
	1990	[7th] GWM 3

Table 5.12 Conferences and Symposia with Papers Relevant to Subsurface Characterization and Monitorings^a (Continued)

Sponsor	Year	Title
NGWA/AGWSE	1991	[8th] GWM 7
	1992	[9th] GWM 13
	1993	[10th] GWM 16
Other NWWA Regional Conferences		
NWWA	1983	Eastern Regional Conference on Ground Water Management Western Regional Conference on Ground Water Management
	1984	Conference on Ground Water Management
	1985	Southern Regional Ground Water Conference Western Regional Ground Water Conference
	1986	Conference on Southwestern Ground Water Issues Focus Conference on Southeastern Ground Water Issues
	1987	Focus Conference on Midwestern Ground Water Issues Focus Conference on Northwestern Ground Water Issues
NGWA	1988	[2nd] Focus Conference on Southwestern Ground Water Issues
	1996	Focus Conference on Northeastern Ground Water Issues
	1998	[3rd] Focus Conference on Southwestern Ground Water Issues: MTBE
Geophysics/Vadose Zone/Karst/Fractured Rock		
NWWA/EPA	1984	[1st] Conference on Surface and Borehole Geophysical Methods in Ground Water Investigations
	1985	[2nd]
	1986	Surface and Borehole Geophysical Methods and Ground Water Instrumentation Conference and Exposition
NWWA/EPA	1983	[1st] Conference on Characterization and Monitoring in the Vadose (Unsaturated) Zone
	1985	[2nd]
	1986	3rd
NWWA	1986	[1st] Conference on Environmental Problems in Karst Terranes and Their Solutions
	1988	2nd
	1991	3rd Conference on Hydrogeology, Ecology, Monitoring and Management of Ground Water in Karst Terranes GWM 10
NGWA	2002	Fractured-Rock Aquifers Conference
Modeling		
NWWA/IGWMC	1984	1st Conference on Practical Applications of Ground Water Models
	1985	2nd
	1986	3rd Conference on Solving Ground Water Problems with Models
	1988	Conference on Geochemical Modeling of Ground Water Contamination
	1989	4th Conference on Solving Ground Water Problems with Models
NGWA/IGWMC	1992	5th GWM9
Miscellaneous NWWA Conferences		
NWWA/AGWSE	1988	Ground Water Geochemistry Conference
	1989	Conference on New Field Techniques for Quantifying Physical and Chemical Properties of Heterogeneous Aquifers
	1990	Cluster of Conferences (Agricultural Impacts on Ground Water Quality; Ground Water Geochemistry; Ground Water Management and Wellhead Protection; Environmental Site Assessments: Case Studies and Strategies) GWM 1
	1991	Environmental Site Assessments: Case Studies and Strategies: The Conference GWM 6
NGWA/AGWSE	1992	[2nd] Environmental Site Assessments: Case Studies and Strategies: The Conference GWM 12
	1998	Animal Feedlot Operations and Ground Water: Issues, Impacts and Solutions
	2000	The Emerging Issues: Endocrine Disruptors, Pharmaceuticals, Arsenic and Radon in Water

Table 5.12 Conferences and Symposia with Papers Relevant to Subsurface Characterization and Monitorings^a (Continued)

Sponsor	Year	Title
	2001	2nd International Conference on Pharmaceuticals and Endocrine Disruptors in Water
Hazardous Materials Control Research Institute Conferences		
HMCRI	1980	1st National Conference on Management of Uncontrolled Hazardous Wastes Sites
	1981	2nd
	1982	3rd
	1983	4th
	1984	5th
	1985	6th
	1986	7th
	1987	8th Superfund '87
	1988	9th Superfund '88
	1989	10th Superfund '89
	1990	11th Superfund '
	1991	12th Hazardous Materials Control (HMC — Superfund '91)
	1992	13th HMC — Superfund '92
	1993	14th
	1994	15th Superfund XV
	1995	16th Superfund XVI
	1996	17th Superfund XVII
	1997	18th Superfund XVIII
HMCRI	1984	1st National Conference on Hazardous Wastes and Environmental Emergencies
	1985	2nd
	1986	3rd National Conference on Hazardous Wastes and Hazardous Materials
	1987	4th
	1988	5th
	1989	6th (HWHM '89)
	1990	7th (HWHM '90)
Regional Hazardous Materials Control Conferences		
HMCRI	1990	HMC — Great Lakes '90
	1991	HMC — Northeast '91
	1992	HMC — South '92
Miscellaneous Conferences		
HMCRI	1992	National R&D Conference on the Control of Hazardous Materials
	1992	Federal Environmental Restoration '92
	1993	Federal Environmental Restoration II and Waste Management
	1994	Federal Environmental Restoration III and Waste Management II

Note: Brackets indicate that number is not included in the title of the published proceedings. GWM indicates that proceedings have been published in NWWA/NGWA's Ground Water Management Series.

^a See list of acronyms in the Preface for full organization names.

Table 5.13 Index to Major References on Existing Environmental Information and Data Management

Topic	References
Existing Information Sources	
Federal Agencies	<u>EPA</u> : U.S. EPA (1988a, 1992, various dates); <u>USGS</u> : Cardin et al. (1986), Dodd et al. (1989), Gilbert and Buchanan (1982), Mercer and Morgan (1982), Rapp et al. (1969), USGS (1979, 1982c, 1982d — ESIS)
Maps/Air Photos	Bauer (1989), FGDC (1992), Makower (1992), Thompson (1979); <u>Aerial Photography</u> : ASTM D5518 (Table A.14)
Geology/Soils	Kaplan (1965), Long (1971), SCS (1991), Ward (1972), Wood (1973)
Ground Water Databases	Kaplan et al. (1985), Orr (1984), Rail (2000), Way et al. (1984); <u>NAWDEX</u> : Edwards (1978), Edwards et al. (1987), Knecht and Edwards (1980), USGS (1982a, 1982b); <u>STORET</u> : U.S. EPA (1986, 1987c); <u>WATSTORE</u> : Baker and Foulk (1980), Hutchinson (1975); <u>Regional Hydrogeology</u> : See Table 2.5
Other Data	Olson (1984 — environmental/natural resources); <u>Geographic</u> : Decker (2001), Walford (2002); <u>Climate</u> : Eder et al. (1989), Hatch (1988); <u>Meteorological Tables</u> : Letetsu (1966), List (1966)
Data Handling	
Data Requirements	<u>Ground Water</u> : U.S. EPA (1987a, 1988b, 1990a); <u>Other</u> : U.S. EPA (1983, 1989a)
Data Management	Kroenke (1977), Olson and Milleman (1985); <u>Environmental Data</u> : Hopke and Massart (1986), Korte (1999 — technical evaluation); <u>Geology</u> : Frizado (1992); <u>Ground Water</u> : Hix (1983), Hoffman (1986), Kaplan et al. (1985), USGS (1984)
QA/QC (EPA Guidance) ^a	<u>Data Quality Assessment/Management</u> : U.S. EPA (1997, 2000c, 2001b); <u>DQO Process</u> : U.S. EPA (1987b, 1993, 2000a, 2000b); <u>Quality Assurance</u> : Barth et al. (1989 — soil), Evans et al. (1987 — ground-water monitoring), Paulson et al. (1988 — survey data), U.S. EPA (1976 — water QA, 1988c — QA terms, 1990b — sampling QA/QC); <u>Quality Assurance Project Plans</u> : Simes (1989), Stanley and Verner (1983), U.S. EPA (1989b, 1991, 1998, 2001a); <u>Standard Operating Procedures</u> : U.S. EPA (1996/T9.10, 2001c)
QA/QC (Other)	<u>Texts/Reports</u> : NAS (1988), NWQL (1986), Taylor (1987), Taylor and Stanley (1985), U.S. Army Corps of Engineers (1990), <u>Papers</u> : Campbell and Mabey (1985), Evans (1986), Kent and Payne (1988), Kirchmer (1983), Lewis (1988), Mateo et al. (1991), Pennino (1988), Starks and Flatman (1991), van Ee and McMillion (1986)

^a See Table 9.11 for major references on QA/QC for chemical analytical procedures.

Table 5.13 References (Appendix F contains references for figure and table sources.)

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* See Preface for information on how to obtain documents from NTIS and Table 5.3 for telephone numbers for the RCRA and Safe Drinking Water Hotlines.

Table 5.14 Index to Major References on Statistics and Sampling Design

Topic	References
General Statistics	
General	Bendat and Piersoll (1986), Benjamin and Cornell (1970), Bethea et al. (1985), Bury (1975), Dixon and Massey (1957), Freund and Wilson (1993), Hoel (1960), Jessen (1978), MacBerthouex et al. (1994), Meyer (1975), Steel and Torrie (1960), Taylor (1994), Wadsworth (1990); <u>Precision and Bias</u> : ASTM (1992)
Sampling Design/Specific Applications	<u>Environmental</u> : Chapman and El-Sharrawi (1990 — point-source pollution), Gilbert (1987 — pollution monitoring), Ginevan and Splitstone (2002 — EQ measurement), Manly (2000), Millard and Neerchal (2000); <u>Geology</u> : Davis (1973), Till (1974); <u>Soils/Solids</u> : Butler (1980), Gy (1979), Pitard (1993), U.S. DOE (1995 — hots spots), U.S. EPA (1989a, 1994 — soil cleanup standards), Webster (1977), Webster and Oliver (1990); <u>Ground Water</u> : Brown (1998), Davis (2000), Gillham et al. (1983), Summers et al. (1985), U.S. EPA (1989b, 1992); <u>Hydrology</u> : Helsel and Hirsch (1992), Riggs (1968); <u>Environmental Biology</u> : Green (1979), EPRI (1985); <u>Environmental Engineers</u> : Berthouex and Brown (2002)
Special Statistical Approaches	<u>Exploratory Data Analysis</u> : Hoaglin et al. (1983), Tukey (1977); <u>Nonparametrics</u> : Hollander and Wolfe (1973), Lehmann and D'Abrera (1975), Seigel (1956)
Time-Series Data	<u>Texts</u> : Chatfield (1984); <u>Ground-Water</u> : Carosene-Link et al. (1993), Close (1989), Gibbons (1987, 1994), Harris et al. (1987), McBean et al. (1988), McNichols and Davis (1988), Montgomery et al. (1987), Nelson and Ward (1981), Pennino (1988), Ross (1993), Rovers and McBean (1981), Schweitzer and Black (1985), Sgambat and Stedinger (1981), Starks (1989), Yevjevich and Harmancioglu (1989)
Spatial Data	Cressie (1991), Diggle (2001); <u>Geostatistics</u> : See below; <u>Factor Analysis</u> : Lawrence and Upchurch (1976)
Analytical Data	Gy (1982); <u>Censored Data</u> : Gilbert (1987), Gilliom and Helsel (1986), Gilliom et al. (1984), Helsel and Gilliom (1986), McBean and Rovers (1984), Porter et al. (1988); <u>Limit of Detection</u> : ACS Committee on Environmental Improvement (1980), ASTM D4210/TA.14, IUPAC (1978), Long and Winefordner (1983), McNichols and Davis (1988), Porter (1986), Porter et al. (1988)
Geostatistics	
Texts	<u>Introductory</u> : Clark (1979); <u>Advanced</u> : David (1977), Matheron (1971), Isaaks and Srivastava (1989), Journal and Huijbregts (1978); <u>Hydrologic Applications</u> : ASCE Task Committee (1990), Bárdossy (1992), Kitandis (1997); <u>Glossary</u> : Olea (1991); <u>Other</u> : Myers (1997)
Applications	<u>Contaminant Characterization</u> : Flatman (1984, 1986), Flatman and Yfantis (1984), Gilbert and Simpson (1985), Journal (1984); <u>Contour Mapping</u> : Olea (1974, 1975); <u>Soil Characterization</u> : Sinclair (1986), Trangmar et al. (1985), Warrick et al. (1986); <u>Ground Water</u> : Delhomme (1978, 1979), Hughes and Lettenmaier (1981), Sophocleous et al. (1982)

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Geophysical and Remote Sensing Techniques

6.1 OVERVIEW OF REMOTE SENSING AND GEOPHYSICAL TECHNIQUES

A wide variety of field investigation techniques are available that provide information about a site with little or no disturbance of the surface and subsurface. In the broadest sense, most of these techniques involve *remote sensing*, the observation of an object or phenomenon without the sensor being in direct contact with the object being sensed. In this chapter, the term *remote sensing* is restricted to airborne photographic and geophysical methods, whereas the term *geophysics* is used loosely to include these remote sensing methods.

Geophysical techniques are used to assess the physical and chemical properties of soils, rock, and ground water based on the response to either (1) various parts of the *electromagnetic* (EM) spectrum, including gamma rays, visible light, radar, microwave, and radio waves (Figure 6.1); (2) *acoustic* or *seismic* energy; or (3) other *potential* fields, such as gravity and the earth's magnetic field.

Historically, geophysical field methods have been mainly the domain of petroleum and mineral exploration geologists. Early successes in the 1970s using electrical methods (measurement of variations in conductivity and resistivity) to locate contaminant plumes and measure the hydrogeologic properties of aquifers have led to the adaptation of a large number of geophysical methods in ground-water contamination investigations.

In the late 1970s, the availability of microcomputers revolutionized the use of field geophysics by allowing on-site processing of the tremendous amount of data generated by most of these techniques. Use of geophysical methods in hydrogeologic studies became so widespread in the 1980s that techniques such as electromagnetic induction, electrical resistivity, seismic refraction, and magnetometry are no longer considered innovative but state of the art. Innovations in these and numerous other geophysical methods continue at a rapid rate.

6.1.1 Uses of Geophysics in Contamination Studies

A wide range of subsurface features can be measured or inferred using geophysical methods. These features can be broadly classified into four groups:

1. *Natural Soil/Geologic/Ground Water Conditions.* Preliminary characterization of soil and geologic stratigraphy (i.e., depth and thickness of layering and lateral changes) and subsurface structure (i.e., depth and topography of unconsolidated material bedrock contact, dip and folding of sediments) is among the primary uses for surface geophysical methods such as ground-penetrating radar, electromagnetic methods, electrical resistivity, and seismic methods. Some other potential uses of these methods for characterizing natural conditions include (1) measurement of depth to

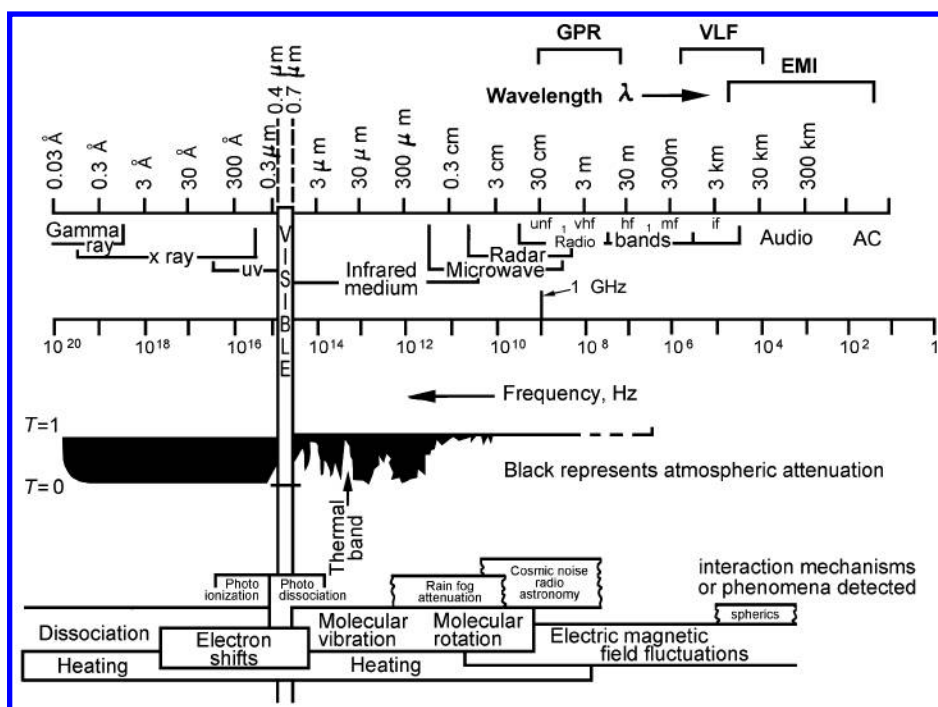


Figure 6.1 The electromagnetic spectrum: the customary divisions and portions used for geophysical measurements (Boulding, 1993a, after Erdélyi and Gálfi, 1988).

water table and aquifer thickness, (2) mapping of clay layers, and (3) detection of subsurface cavities and sinkholes.

2. *Contaminated Ground Water.* When contaminants in ground water create conductive plumes of leachate (i.e., landfills, injected brines, saltwater intrusion), electromagnetic and resistivity are good methods for preliminary characterization of the extent and direction of flow of a plume. Where contaminant plumes are relatively near the surface, the depth of the top of the plume serves as an indicator of the thickness of the vadose zone.
3. *Buried Wastes.* Ground-penetrating radar, electromagnetic induction, and electrical resistivity can be good methods for preliminary delineation of the location and boundaries of bulk wastes and nonmetallic containers. Electromagnetic induction, metal detectors, and magnetometry are primary methods for detection of buried metallic containers (except that magnetometry will not detect nonferrous metals).
4. *Other Anthropogenic Features.* Other subsurface anthropogenic features that can be detected by surface geophysical methods include location of pipes, cables, tanks, and abandoned well casings. Loose fill in trenches associated with buried utilities may form permeable pathways for preferential flow of contaminants in the subsurface. Magnetometry, metal detection, electromagnetic induction, and ground-penetrating radar are the surface geophysical methods that are primarily used for these applications.

The greatest benefits of geophysical methods come from early use. These methods are typically nondestructive, less risky, cover more area spatially and volumetrically, and require less time and cost than site characterization using monitoring wells. On the other hand, great skill is required in interpreting the data generated by these methods, and their indirect nature creates uncertainties that can only be resolved by direct observation. Consequently, preliminary site characterization by geophysical methods is usually followed by direct observation through the installation of monitoring wells.

Airborne and surface geophysical methods can reduce the number of monitoring wells that must be drilled to adequately characterize a site, which can result in significant cost savings. Figure

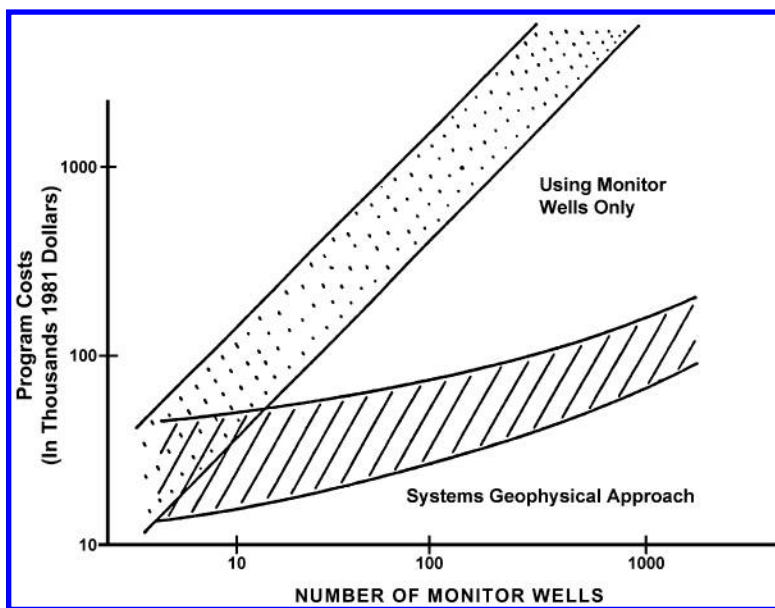


Figure 6.2 Cost comparison curve for hazardous waste site investigations: geophysics vs. monitoring wells only (Benson et al., 1984).

6.2 illustrates potential cost savings from using geophysical methods to help site monitoring wells, compared to the use of monitoring wells only. When only a few monitoring wells are involved, the costs of the two approaches may be comparable, but when the number of required monitoring wells exceeds 10 or so, geophysical methods become increasingly more cost-effective as the number of wells increases.¹

6.1.2 General Characteristics of Geophysical Methods

Geophysical investigation techniques can be broadly grouped into three categories: (1) airborne remote sensing, (2) surface, and (3) borehole or downhole methods. Each of these categories has numerous specific techniques, and a specific technique may have a number of variants. Table A.1 (Summary Information on Remote Sensing and Surface Geophysical Methods) and Table A.2 (Characteristics of Borehole Logging Methods) present information on more than 70 specific methods. The rest of this chapter focuses on the more commonly used methods.

Remote sensing and airborne geophysics do not involve direct contact with the object being observed and usually involve airborne instrumentation (see [Section 6.2](#)). As the names imply, surface methods involve wave generators and sensors at or near the ground surface (see [Section 6.3](#)), and downhole methods involve sensing methods below the surface. Some specific techniques may be used in more than one way. For example, electromagnetic induction ([Section 6.3.1](#)) can be used from an airplane, on the ground surface, and in boreholes.

Most of the techniques discussed in this chapter operate in a portion of the electromagnetic spectrum. Electromagnetic radiation can be described in terms of *wavelength*, the distance between two crests of the wave, and *frequency*, the number of waves measured passing a certain point in the medium in the course of 1 sec (cycles per second). Airborne remote sensing methods tend to sense higher frequencies (infrared through ultraviolet), whereas surface geophysical methods

¹ Note that this figure applies to installation of permanent monitoring wells. Surveys using push technologies, as discussed in [Section 9.1.2](#), provide many of the benefits of geophysical methods with the added benefit of allowing direct sampling of the subsurface.

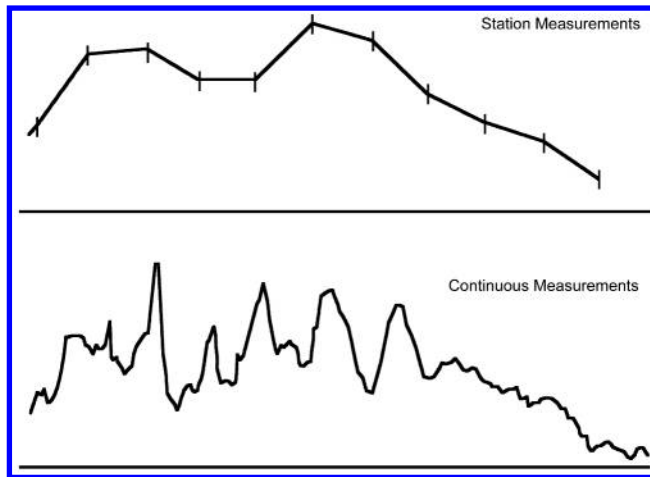


Figure 6.3 Discrete sampling vs. continuous geophysical measurements (Boulding, 1993a, after Benson et al., 1984).

generally sense the response of subsurface materials to lower frequencies in the EM spectrum (Figure 6.1).

Geophysical methods tend to measure a larger volume of the subsurface than monitoring wells, thereby increasing the volume sampled for a given measurement. This is usually an advantage, but can be a disadvantage if a feature or anomaly is so small that it may escape detection in a larger sampled volume. Data from these methods may be acquired in the form of (1) *profiles*, which record changes in measured properties in a linear transect along the ground surface, or (2) *soundings*, which measure vertical changes in the measured properties.

Profile measurements can be either *stationary* or *continuous*. Stationary, or station, measurements are taken at discrete intervals, whereas continuous methods measure subsurface parameters continuously along a survey line. Figure 6.3 shows the difference in output from the two types. The figure shows that continuous measurements, where feasible, provide better resolution, but most traditional geophysical techniques involve station measurement. Continuous methods, such as EM induction, are typically limited to a depth of 15 m or less, but are still preferred when applicable, since they can approach 100% site coverage.

6.2 AIRBORNE REMOTE SENSING

Although all geophysical methods involve remote sensing in some fashion, the term is used here to apply to airborne instrumentation. Table 6.1 presents a summary description and listing of hydrogeologic applications for six remote sensing techniques. Figure 6.4 shows features that can be identified in the portions of the spectrum that are sensed using airborne methods.

6.2.1 Visible and Near-Infrared Aerial Photography

Aerial photographs, which record the visible portion of the electromagnetic spectrum, are by far the most common form of remote sensing and are basic to any geologic or hydrogeologic investigation. Much information can be obtained from stereopairs of black-and-white air photos, which provide a three-dimensional image of the surface when viewed with a stereoscope. Patterns of vegetation, variations in gray tones in soil and rock, drainage patterns, and linear features allow preliminary interpretations of geology, soils, and hydrogeology. All air photo interpretations should

Table 6.1 Use of Airborne Sensing Techniques in Hydrogeologic and Contaminated Site Studies

Method	Description	Applications
Visible and near infrared	Aerial photographs (black and white, color, false color, infrared, multispectral); imaging limited to surface features	Air photo interpretation of geologic and surface hydrologic features, fracture-trace analysis, soil moisture patterns, and vegetation (infrared)
Photographic ultraviolet	Aerial photographs using special film and filters for sensing reflected ultraviolet radiation	Mapping of oil spills on surface water bodies; sometimes used for geologic mapping of carbonate formations
Thermal infrared	Scanners used to detect infrared radiation beyond the range of infrared photography	Routinely used to detect ground-water discharge into rivers, lakes, and the sea; detects variations in soil moisture content (seepage from leach fields and underground storage tanks), evaporation, and thermal properties
SLAR	Creates a continuous radar image (reflected radio frequency pulses) of the ground surface.	Applications similar to those of air photos; can distinguish grain size in alluvium if there is no interference from vegetation; can also be used for fracture-trace analysis
Low-frequency AEMs	Uses a low-frequency electromagnetic wave transmitter and receiver that responds to changes in the ground electrical conductivity	Detects variations in soil and rock types, variations in ground-water salinity, location of shallow subsurface aquifers and deeper brine contaminated aquifers
Aeromagnetic	Measures the earth's total magnetic field	Primarily used in petroleum and mineral exploration to assist with geological mapping and structural interpretations; also used to locate abandoned wells with metallic casings

Source: Boulding (1993a).

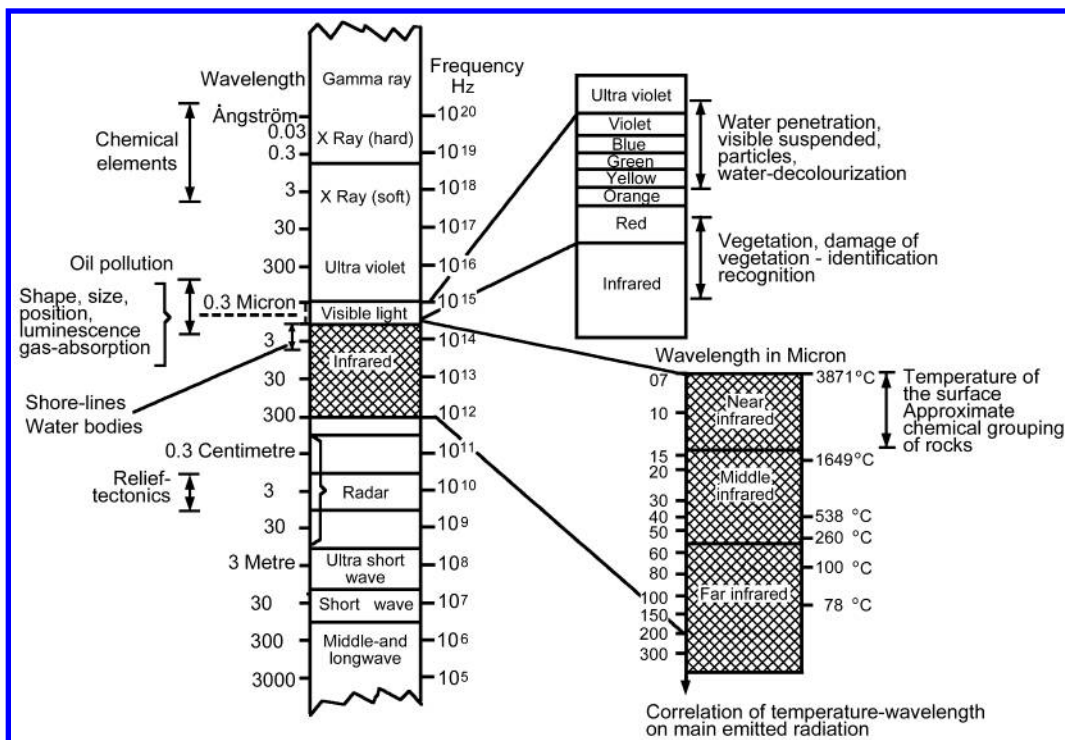


Figure 6.4 Factors and phenomena influencing the radiation of electromagnetic waves (Boulding, 1993a, after Erdélyi and Gálfi, 1988).

be field checked and revised where “ground truthing” indicates features that were missed or incorrectly delineated.

Photogrammetric techniques using stereoscopic (overlapping) aerial photographs are often the cheapest way to produce accurate topographic maps (1- or 2-ft contour intervals) for site-specific investigations.

Black-and-white (also called panchromatic) air photos are available from various federal agencies for almost any location in the U.S. and are the cheapest type of air photo to obtain. Black-and-white photographs are reported most frequently as being useful in ground-water contamination studies. Other types of images that can be obtained, usually at greater expense, include:

- *True color*, which records all colors in the visible spectrum as they appear to the naked eye.
- *Color infrared film*, which records yellows and reds as green and the near infrared (not visible to the eye) as red. Since vegetation reflects near-infrared radiation, this image is especially useful for observing vegetation patterns. Other types of images that record or display colors differently than they are perceived by the eye (called *false color*) can be created in a similar fashion.
- *Photographic ultraviolet*, which uses special film and filters to record UV energy. Oil and carbonate minerals are fluorescent in UV bands when photostimulated by sunlight. A disadvantage of UV photography is that UV wavelengths are scattered in the atmosphere and result in a low-contrast image, especially when dust or haze is present.
- *Multiband* (also called *multispectral*) images use multiple lenses and filters to record simultaneous exposures of different portions of the visible and near-infrared spectrum of the same area on the ground. Images can also be recorded electronically using a multispectral scanning system.

Air photos often reveal linear features called fracture traces that indicate zones of relatively higher permeability in the subsurface. Fracture-trace analysis using air photos can provide preliminary information on possible preferential movement of contaminants (Parizek, 1976).² Aerial photography can also be a valuable tool in documenting preexisting physical conditions and monitoring the progress of cleanup operations at hazardous waste sites (Finkbeiner and O’Toole, 1985).³ Color infrared photography is most useful where contamination results in vegetation changes such as failed septic tank absorption systems (Farrell, 1985),⁴ fertilizers, oil pollution, and natural gas leaks (Švoma and Pyšek, 1985).⁵

6.2.2 Other Airborne Remote Sensing Techniques

Table 6.1 describes four other aerial remote sensing techniques that may have applications in hydrogeologic studies. *Thermal infrared* scanning can detect ground-water discharge into surface waters by sensing temperature differences in the ground and surface water. Contaminant plumes often differ in temperature from the surrounding ground water and may also be detected using this method.

Airborne geophysical methods such as *side-looking airborne radar* (SLAR), *airborne electromagnetic methods* (AEMs), and *aeromagnetics* have not been widely used in ground-water contamination studies, although potential exists for their use in regional water quality studies. A special

² Parizek, R.R. 1976. On the Nature and Significance of Fracture Traces and Lineaments in Carbonate and Other Terranes. In: Karst Hydrology and Water Resources, Vol. 1, V. Yevjevich (ed.), Water Resources Publications, Fort Collins, CO, pp. 3-1 to 3-62.

³ Finkbeiner, M.A. and M.M. O’Toole. 1985. Application of Aerial Photography in Assessing Environmental Hazards and Monitoring Cleanup Operations at Hazardous Waste Sites. In: Proceedings of the 6th National Conference on Management of Uncontrolled Hazardous Waste Sites, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 116–124.

⁴ Farrell, S.O. 1985. Evaluation of Color Infrared Aerial Surveys of Wastewater Soil Absorption Systems. EPA/600/2-85/039 (NTIS PB85-189074).

⁵ Švoma, J. and A. Pyšek. 1985. Photographic Detection of Groundwater Pollution. In: Hydrological Applications of Remote Sensing and Remote Sensing Data Transmission, B.E. Goodison (ed.), International Association of Hydrological Sciences Publication 145, pp. 561–567.

feature of SLAR is its ability to distinguish grain size in alluvium. This technique requires unvegetated surfaces, a condition that is most likely to occur in arid areas.

Surface, rather than airborne, electromagnetic methods are generally better adapted to site-specific ground-water contamination studies, since the spatial resolution of airborne EM methods (on the order of several tens of meters) is usually too coarse for contamination investigations. The U.S. EPA has been supporting research on the use of airborne electromagnetics to locate areas of near-surface brine contamination in the Brookhaven oil field in Mississippi (Smith et al., 1989).⁶ Aeromagnetic surveys have been used as a complement to other methods to locate abandoned wells (Frischknecht, 1990).⁷

6.3 SURFACE GEOPHYSICAL METHODS

Surface geophysical methods have been widely used in ground-water contamination studies for the reasons discussed in [Section 6.1.1](#). Eight major geophysical methods are currently being used at contaminated sites, in the following order of approximate frequency of use: (1) electromagnetic induction, (2) electrical resistivity, (3) magnetometry, (4) ground-penetrating radar, (5) seismic refraction, (6) shallow seismic reflection, (7) gravimetrics, and (8) thermal sensing. [Table 6.2](#) presents a brief summary description of each method and its applications to ground-water contamination studies. The following sections provide additional information on each method. [Section 6.6](#) provides some comparative information on the six most commonly used methods.

6.3.1 Electromagnetics

Electromagnetic methods measure the electrical conductivity of the subsurface. Although most geophysical methods use electromagnetic principles, common usage of the term *EM* in the geophysical industry implies measurement of subsurface conductivities at relatively low frequencies ([Figure 6.1](#)). Electrical conductivity is a function of the type of soil and rock, its porosity, permeability, and the fluids that fill the pore space. The conductivity (measured as specific conductance — millimhos per meter) of the pore fluids usually dominates the measurement, especially when dissolved species are present in contaminated water. Consequently, EM is an excellent technique for mapping contaminant plume boundaries, as well as a variety of other subsurface features with contrasting electrical properties.

Electromagnetic induction (EMI) and *metal detectors* are the most commonly used electromagnetic methods used in contamination studies. [Figure 6.5](#) shows the basic principle of operation of an EMI instrument: a transmitter coil generates a sinusoidal electromagnetic field that induces eddy currents in the earth below the instrument. A receiver coil then intercepts both the primary and the secondary electromagnetic fields created by the eddy current loops and produces an output voltage that is corrected for the primary field and the loop geometry and spacing. This voltage, within limits, is linearly related to subsurface conductivity. The reading represents the weighted cumulative sum of the conductivity variations from the surface to the effective depth of the instrument. The effective depth for EMI is determined by the geometry and spacing of the transmitting and receiving coils, with 60 m representing a typical maximum depth. Readings to shallow depths can be made continuously since the coils are rigidly connected, whereas greater depth penetration requires stationary measurements.

⁶ Smith, B., W. Heran, R. Bisdorf, and A.T. Mazzella. 1989. Evaluation of Airborne Geophysical Methods to Map Brine Contamination. EPA/600/4-89/003, U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, NV.

⁷ Frischknecht, F.C. 1990. Application of Geophysical Methods to the Study of Pollution Associated with Abandoned and Injection Wells. In: Proceedings of a U.S. Geological Survey Workshop on Environmental Geochemistry, B.R. Doe (ed.), U.S. Geological Survey Circular 1033, pp. 73–77.

Table 6.2 Major Surface Geophysical Methods for Study of Subsurface Contamination

Method	Description	Hydrogeologic Applications
EMI, TDEM, metal detector (MD) (Section 6.3.1)	<p>EMI: Uses a transmitter coil to generate currents that induce a secondary magnetic field in the earth that is measured by a receiver coil. Well suited for areal searches.</p> <p>TDEM: Uses a transmitter loop placed on the ground to create a descending eddy current upon termination of current flow and a receiver coil that measures the decaying magnetic field.</p> <p>MD: Specialized EMI instruments designed to sense increased conductivity resulting from buried ferrous or nonferrous metals.</p>	<p>Can be used to map a wide variety of subsurface features, including natural hydrogeologic conditions, delineation of contaminant plumes, rate of plume movement, buried wastes, and other artificial features (e.g., buried drums, pipelines).</p> <p>EMI: Depth of penetration is typically up to 60 m, but depths to 200+ m are possible.</p> <p>TDEM: Penetration of more than 2000 m is possible.</p> <p>MD: Maximum depth of 3 m for single drum, and 6 m for large pile of metallic material.</p>
DC electrical resistivity (Section 6.3.2)	Measures the resistivity of subsurface materials by injecting an electrical current into the ground by a pair of surface electrodes and measuring the resulting potential field (voltage) between a second pair of electrodes.	Similar to electrical conductivity (see above), except not widely used to detect metallic objects, for which magnetic and EMI methods are more effective. Better for depth sounding than frequency domain EMI.
Seismic refraction and reflection (Section 6.3.3)	Uses a seismic source (commonly a sledge hammer), an array of geophones to measure travel time of the refracted/reflected seismic waves, and a seismograph that integrates the data from the geophones.	Can be used to define the thickness and depth to bedrock or water table, thickness of soil and rock layers, and their composition and physical properties; may detect anomalous subsurface features such as pits and trenches. ^a
Magnetometry (Section 6.3.4)	Uses a magnetometer to measure the intensity of the earth's magnetic field.	Used to locate buried metal drums that may be sources of soil and ground-water contamination.
GPR (Section 6.3.5)	Uses a transmitter coil to emit high-frequency radio waves that are reflected off subsurface changes in electrical properties (typically density and water content variations) and detected by a receiving antenna.	Can map soil layers, depth of bedrock, buried stream channels, rock fractures, cavities in natural settings, and buried waste materials. Maximum depth of penetration under favorable conditions is around 25 m. Hundreds of meters penetration may be possible in highly resistive materials (salt or ice).
Gravimetry (Section 6.3.6)	Uses one or more of several types of instruments that measure the intensity of the earth's gravitational field.	Can be used to estimate depth of unconsolidated material over bedrock and boundaries of landfills, which have a different density than natural soil material. Microgravity surveys may be able to detect subsurface cavities and subsidence voids.
Thermal sensing (Section 6.3.7)	Uses temperature sensor anomalies in the soil or surface water.	Can be used to delineate shallow ground-water flow systems, buried valley aquifers, recharge and discharge zones, zones of high permeability, leakage beneath earthen dam embankments, and location of solution channels in karst.

^a High-resolution shallow seismic reflection is increasingly being used as an alternative to seismic refraction. Minimum depth resolution is typically 10 m, but it can be as shallow as 3 m.

Source: Boulding (1993a).

Metal detectors, EM instruments that have been designed to respond to the electrical conductivity of metals, are commonly used to locate buried metals at uncontrolled hazardous waste sites. They have the advantage of detecting nonferrous metals such as aluminum and copper, which cannot be detected with magnetometers (Section 6.3.4).

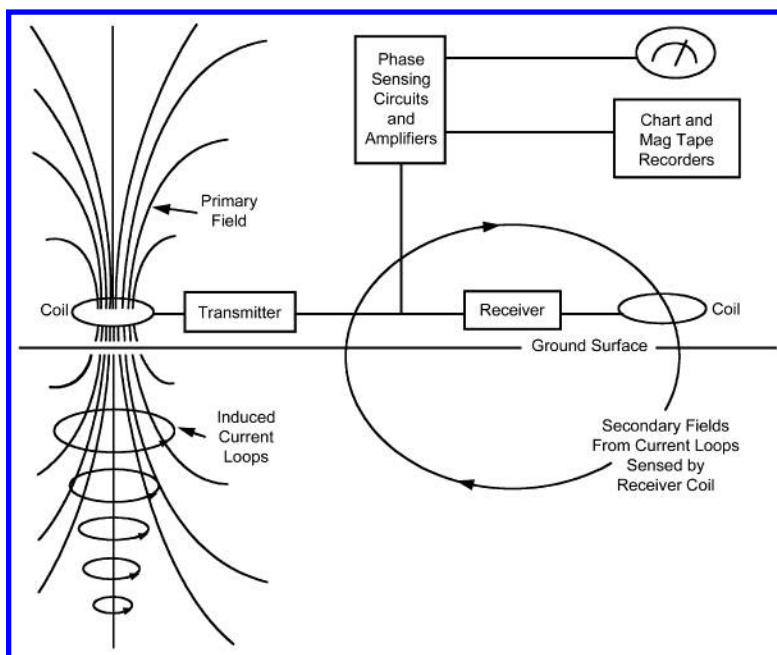


Figure 6.5 Electromagnetic induction principle of operation (Boulding, 1993a, after Benson et al., 1984).

Other potentially useful electromagnetic methods include:

- *Time domain electromagnetic* (TDEM), also called *transient EM*, instruments, which measure the response of the subsurface to a decaying induced current. These instruments can measure to depths exceeding 2000 m and are especially useful for detecting freshwater–saltwater interfaces and brine contamination associated with petroleum production.
- *Very low frequency (VLF) resistivity*, which measures the ratio of electric to magnetic fields generated by military communication transmitters. Potential uses are similar to those of EMI instruments.
- *Magnetotelluric* methods, which include a variety of techniques that measure earth response to natural electrical and magnetic currents in the subsurface. These methods, especially the *controlled source audiomagnetotelluric* (CSAMT) method, which uses a remote transmitter to create a signal with known characteristics, have some potential for regional ground-water investigations and detection of deep, conductive contaminant plumes.⁸

6.3.2 Resistivity and Other Electrical Methods

The electrical resistivity method (ER, for electrical resistance) measures the resistance to flow of electricity in subsurface material. Other terms used to describe this method include direct current (DC) resistivity, galvanic resistivity, and geoelectric resistivity. Resistance is the reciprocal of conductance. Consequently, applications of ER in hydrogeologic studies are similar to those of EM methods, with site-specific conditions determining which may be the preferred method (Section 6.6). In contrast to EM, which does not require direct contact with the ground surface, ER involves the placement of electrodes, called *current electrodes*, on the surface for injection of current into the ground. This current is measured by a voltmeter between two other electrodes, called *potential*

⁸ Tinlin, R.M., L.J. Hughes, and A.R. Anzzolin. 1988. The Use of Controlled Source Audio Magnetotellurics (CSAMT) to Delineate Zones of Ground-Water Contamination. In: Ground-Water Contamination: Field Methods, A.G. Collins and A.I. Johnson (eds.), ASTM STP 963, American Society for Testing and Materials, Philadelphia, pp. 101–118.

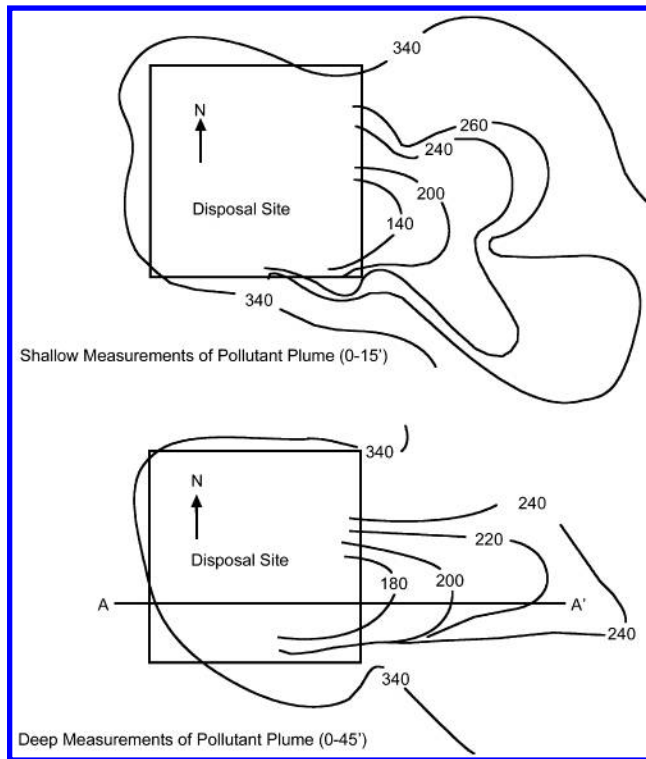


Figure 6.6 Resistivity soundings showing extent of a landfill contaminant plume (Boulding, 1993a, after Benson et al., 1984).

electrodes. Apparent resistivity (measured in ohm-meters or ohm-feet) can be calculated from the spacing of the electrodes, the current injected, and the voltage.

DC resistivity methods are identified according to the arrangement of current and potential electrodes, with *Wenner*, *Schlumberger*, and *dipole-dipole* arrays being the most commonly used today. Increasing the spacing between the current and potential electrodes increases the depth of the sounding measurement (in the Wenner array the spacing should be one to two times the depth of interest). *Tripotential* DC resistivity is a relatively new method that involves taking readings from three electrode arrays (Wenner, dipole-dipole, and bipole-bipole) at each station and can allow resolution of ambiguities from single-array readings. *Azimuthal* resistivity measures the variations in electrical response to changes in the orientation of electrode arrays at a single location and is especially useful to detection of the orientation of subsurface fractures and impermeable caps at waste disposal sites.

Figure 6.6 shows use of resistivity measurements in delineating a leachate plume from a landfill by isopleths of equal resistance measured in ohm-feet. Since landfill leachate contains ions that decrease the resistivity of the ground water, the lower-value isopleths in Figure 6.6 delineate the most contaminated areas (140 Ω -ft in the upper map and 180 Ω -ft in the lower map). In the figure, the deep measurements (0 to 45 ft) include an averaging of the resistivity of the shallow measurements and the resistivity of the 15- to 45-ft depth interval.

Conductance and resistance are reciprocals, so the output of both EM and ER methods can be expressed in terms of either units (1000 mmhos/m = 1 Ω -m). The published literature on both methods sometimes uses these units interchangeably; thus EM measurements may be reported in terms of resistivity or ER measurements in terms of conductivity. The method used to measure subsurface properties (induction for EM, and current injection by electrodes for ER) will indicate the technique, not necessarily the units in which the measurements are reported. EM and ER

methods are by far the most widely used surface geophysical techniques in ground-water contamination studies.

Other, less commonly used electrical methods include:

- *Self-potential* (SP), which uses electrodes to measure natural electrical potentials developed locally in the subsurface. Several types of natural potentials can be measured by this method. *Spontaneous polarization* is a natural voltage difference that occurs as a result of electric currents induced by disequilibria within the earth. *Streaming potential* is an electrokinetic effect related to movement of fluid containing ions through the subsurface. The method is especially useful for detecting conduit flow in karst limestone (Section 7.5.4 and Figure 7.16) and leaks in impoundments and lined ponds. Birch (1998)⁹ has described a method for imaging water tables by linear filtering of SP profiles when the depth to water table is known for at least one point. An advantage of self-potential methods is that instrumentation is relatively simple and inexpensive.
- *Induced polarization* (IP), which measures the electrochemical response of subsurface material (primarily clays) to an injected current. Equipment and field procedures are similar to those for DC resistivity surveys but are slower and more expensive. *Complex resistivity*, a variant of IP that uses a larger frequency spectrum, has been used with some success experimentally to detect organic contaminant plumes.

6.3.3 Seismic Refraction and Shallow Seismic Reflection

Seismic reflection techniques have been used for many years by the petroleum industry to obtain stratigraphic and structural data on deeply buried sediments. In contrast, seismic *refraction* techniques are designed to obtain data on the near surface (typically to about 30 m). Seismic refraction provides data on the refraction of seismic waves at the interface between subsurface layers, and their travel time within the layers. Properly interpreted, the refraction data allow estimates of the thickness and depth of unconsolidated materials and bedrock and their properties. Lateral facies changes in aquifer material can also be mapped with this method.

Figure 6.7a shows a field layout for seismic refraction measurements. A seismic source (usually a hammer for near-surface investigations) creates direct compressional waves and refracted waves that are sensed by an array of geophones. The seismograph records the time of arrival of all waves, using the moment the hammer hits the ground as time zero. The processing and interpretation of seismic refraction data require a great deal of skill. Figure 6.7b shows the required steps. First, the seismic signal is recorded on paper or on magnetic tape. A single-channel seismograph plots the waveform against time (milliseconds) from a single geophone, and a multichannel instrument records waveforms from multiple geophones (Figure 6.7b). Then, travel time is plotted against source-to-geophone distance to produce a time/distance (T/D) plot. Finally, line segments, slope, and break points in the T/D can be analyzed to identify the number of layers and depth of each layer.

Relatively recent advances in instrumentation for high-resolution seismic *reflection* allows high-resolution mapping of depth to bedrock where unconsolidated material is deeper than 10 to 30 m, and mapping of stratigraphy and rock type at greater depths. More recent advances in seismic reflection amplitude analysis have allowed mapping of areas of free-phase carbon tetrachloride, a DNAPL, at a depth of around 100 ft.¹⁰

6.3.4 Magnetometry

Magnetic measurements have long been used to map regional geologic structures and in mineral exploration. Their main use in ground-water contamination studies is to locate buried metal drums that may be a source of contamination. A magnetometer locates ferrous metals (iron, steel, and

⁹ Birch, F.S. 1998. Imaging the Water Table by Filtering Self-Potential Profiles. *Ground Water* 36:779–782.

¹⁰ Temples, T.J., M.G. Waddell, W.J. Domoracki, and J. Eyer. 2001. Noninvasive Determination of the Location and Distribution of DNAPL Using Advanced Seismic Reflection Techniques. *Ground Water* 39:465–474.

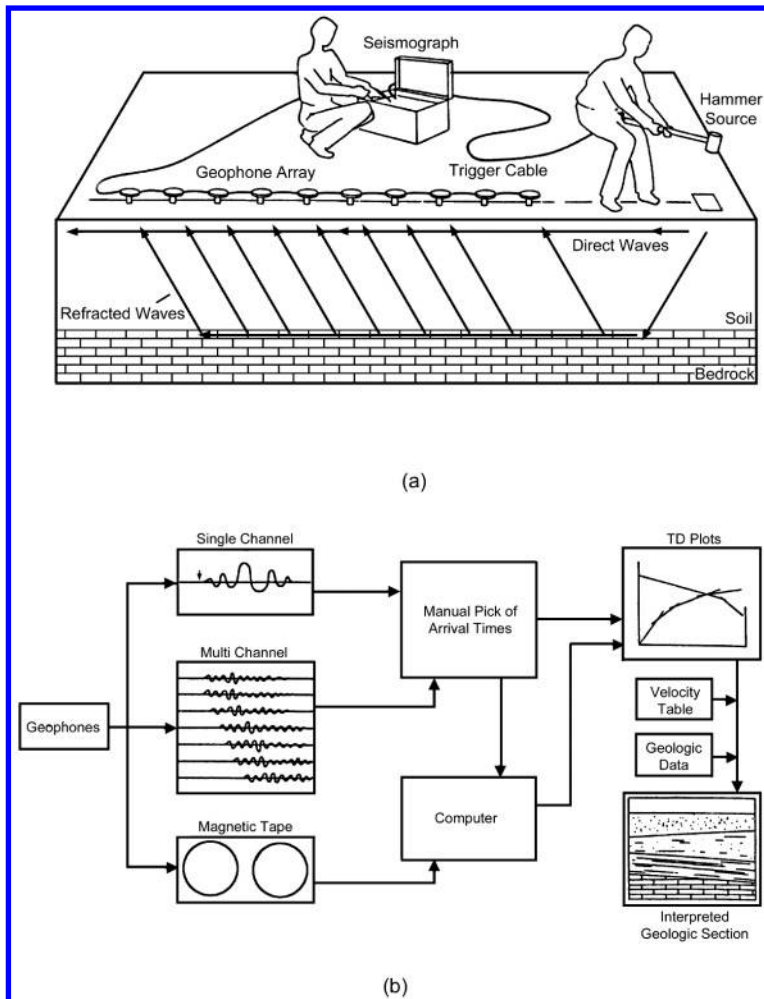


Figure 6.7 Seismic refraction: (a) field layout of a 12-channel seismograph; (b) steps in processing and interpretation of seismic refraction data (Boulding, 1993a, after Benson et al., 1984).

nickel) in drums, buried pipelines, etc., by measuring local perturbations in the strength of the earth's magnetic field. Single 55-gal drums can be sensed up to a depth of 6 m, and piles of drums up to 20 m.

6.3.5 Ground-Penetrating Radar

Geophysical methods using the radio- and microwave portion of the electromagnetic spectrum probably have the most confusing terminology of any surface method, although the term *ground-penetrating radar* has now gained fairly wide acceptance. Other names that can be found in the literature on this method include electromagnetic subsurface profiling, electromagnetic pulse radar, pulsed microwave, pulsed radio frequency, ground-piercing radar, ground-probing radar, and sub-surface impulse radar.

In the mid-1960s and early 1970s, the military provided the impetus for development of ground-penetrating radar (GPR), primarily for detecting land mines and subsurface tunnels. Since then, GPR has been used increasingly in the mining industry and in soil and contaminant investigations to characterize depth to water table, soil horizon and lithologic contacts, cavities, faults, and bedding joints and planes in rocks, and to detect boundaries of buried trenches and containers.

GPR uses a small microwave transmission antenna to radiate high-frequency radio waves into the subsurface and a receiving antenna to record variations in the reflected return signal. Dragging the antennae along the ground surface creates a continuous profile that gives the greatest resolution of all the surface geophysical methods discussed in this book. However, the depth of penetration is generally less than that with other methods (1 to 15 m) and is limited by fluids, soils with high electrical conductivity, and fine-grained materials. GPR has become a popular method for detection of trench boundaries and masses of buried waste at uncontrolled hazardous waste sites where depths of burial have not been too great. Lane et al. (2000)¹¹ found GPR to be problematic for detecting NAPLs in fractured rocks, but considered it a potential tool for monitoring pumping and tracer tests, and changes in site hydrologic conditions. Tsoflias et al. (2001)¹² successfully used GPR for real-time monitoring of pumping tests in a fracture carbonate aquifer. Sneddon et al. (2000/T6.8) used GPR to estimate saturation values for dense nonaqueous phase liquids in an isolated test cell subjected to a controlled release of perchloroethylene. The authors conclude that using full-waveform GPR modeling to determine and map changes in DNAPL saturation values over time can provide valuable inputs to three-dimensional, multiphase fluid flow modeling programs.

6.3.6 Gravimetrics

Gravimetry involves measurement in variations in the intensity of the earth's gravitational field (expressed as acceleration in centimeters per second squared, or Gals). Three principle classes of instruments are used in conventional gravity measurements: torsion balance, pendulum, and gravity meter or gravimeter. All can detect anomalies as small as one ten millionth (milligals — 10^{-3} Gals) of the earth's gravitational field. *Microgravimeters*, measuring in units of microgals (10^{-6} Gals), are sufficiently sensitive that they can delineate cavities in the subsurface. This type of instrument usually is used in hydrogeologic and contaminated site investigations.

Station measurements along a transect or on a grid require great care in setting up the instrument, and the elevation of each station must be carefully surveyed. Gravity data obtained in the field must be corrected for elevation, rock density, latitude, earth tide variations, and the influence of surrounding topographic variations. After corrections, measurements are plotted as Bouger anomaly maps, which look like topographic contour maps, and are interpreted in terms of the size, shape, and position of subsurface structures.

The most common uses of gravity measurements include detecting bedrock valleys buried by unconsolidated glacial materials and conducting regional-scale ground-water investigations. Gravity methods are sometimes used for more site-specific investigations of contaminated sites. For example, Roberts et al. (1989)¹³ obtained gravity data at a landfill in Tippecanoe County, Indiana, and compared these with gravitational estimates based on prelandfill topographic data to determine density variations within the fill material.

6.3.7 Thermal Methods

Because water has a high specific heat capacity compared to most natural materials, its temperature changes slowly as it migrates through the subsurface. Consequently, shallow-earth temperatures can be related to the occurrence and flow of ground water (Figure 6.8). In recharge areas, ground water tends to be warmer than the normal soil temperature. This effect can be used to detect

¹¹ Lane, J.W., Jr., M.L. Buursink, F.P. Haeni, and R.J. Versteeg. 2000. Evaluation of Ground-Penetrating Radar to Detect Free-Phase Hydrocarbons in Fractured Rocks: Results of Numerical Modeling and Physical Experiments. *Ground Water* 38:929–938.

¹² Tsoflias, G.P., T. Halihan, and J.M. Sharp, Jr. 2001. Monitoring Pumping Test Response in a Fractured Aquifer Using Ground-Penetrating Radar. *Water Resources Research* 37:1221–1229.

¹³ Roberts, R.G., W.J. Hinze, and D.I. Leap. 1989. A Multi-Technique Geophysical Approach to Landfill Investigations. In: *Proceedings of the 3rd National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods*, National Water Well Association, Dublin, OH, pp. 797–811.

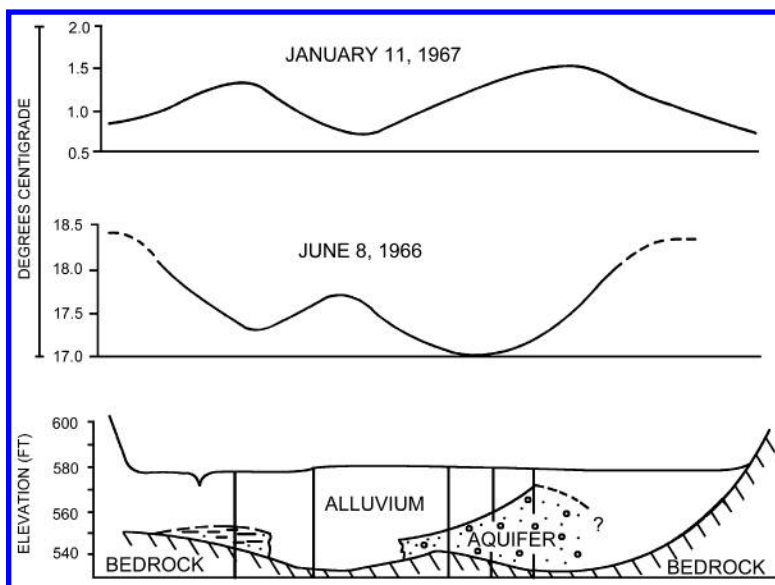


Figure 6.8 Temperature profiles of a discontinuous sand and gravel aquifer within fine-grained alluvium (Boulding, 1993b, after Cartwright, 1968).

contaminant plumes. For example, Cartwright and McComas (1968)¹⁴ used soil temperature surveys at several landfills in northeastern Illinois. These surveys indicated the presence of a halo of higher temperatures around the landfills and indicated areas of surface recharge. Shallow geothermal measurements are usually made by measuring subsurface temperatures at a selected depth (up to 40 in.) at numerous stations over a short time span.

6.4 BOREHOLE GEOPHYSICS

Borehole geophysics is the science of recording and analyzing continuous or point measurements of physical properties made in wells or test holes. Most specific borehole geophysical techniques have long been in use by the petroleum industry, where holes being logged are usually deep and filled with drilling muds or saline water. Many of these techniques are not suitable or must be adapted for use in freshwater aquifers, which are the focus of near-surface hydrogeological investigations. Nevertheless, suitable borehole geophysical methods can greatly enhance the geologic and hydrogeologic information obtained from water supply or monitor wells.

Rarely is a single logging method used; many logs require other logs for interpretation. Even when they are not mandatory, multiple logs may interact synergistically to provide more information than individual logs. For example, the minerals gypsum and anhydrite can be distinguished by interpreting gamma and neutron logs together. Figure 6.9 shows typical responses of three electrical logs (spontaneous potential, single-point resistance, and long-normal resistivity — see Section 6.4.1), two nuclear logs (gamma and neutron — see Section 6.4.2), and three other types of logs (acoustic velocity, caliper, and temperature — see Sections 6.4.3 and 6.4.4). In Figure 6.9, the individual logs do not always show changes with a change in lithology, but for individual strata, one or more logs show changes in measured properties at the top and bottom of the formation. As with surface geophysical methods, most downhole methods require considerable training and skill in recording and interpreting data.

¹⁴ Cartwright, K. and M.R. McComas. 1968. Geophysical Surveys in the Vicinity of Sanitary Landfills in Northeastern Illinois. *Ground Water* 6(5):912–918.

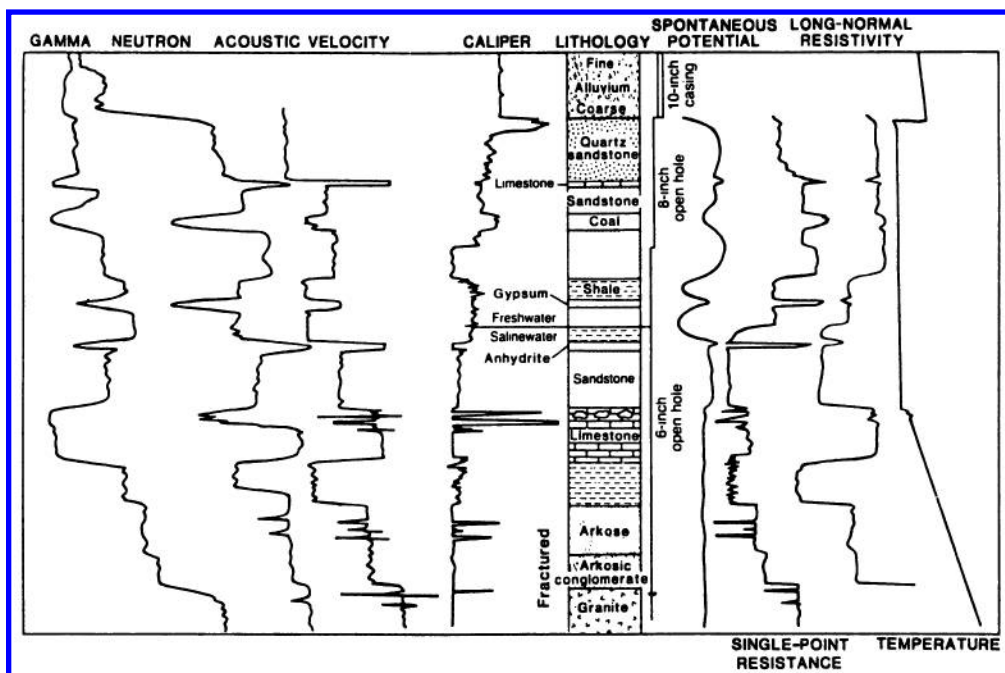


Figure 6.9 Typical response of a suite of hypothetical geophysical well logs to a sequence of sedimentary rocks (Boulding, 1993a, after Keys, 1990).

A bewildering number of specific borehole logging methods are available. Table A.2 provides some summary information on more than 40. Equally confusing to the uninitiated is the fact that the same logging technique may be called by several different names. The next three sections describe briefly the major types of logging techniques that have potential for applications of hydrogeologic studies. Section 6.4.5 and Table 6.7 provide some information on specific applications of individual borehole methods.

6.4.1 Electrical and Electromagnetic Logging Methods

Electrical logging measures the flow of electric current in and adjacent to the well. Table 6.3 describes eight major types of electrical logs and their potential for hydrogeologic applications. Spontaneous potential logs, one of the most commonly used electrical logs, simply record the changes in current flow that result from changes in lithology (Figure 6.10).

Single-point resistance, normal, focused, and lateral resistivity logs all measure resistivity using the same principles as surface resistivity measurements. Resistivity logging methods have numerous variants depending on electrode configurations and spacings (see also Section 6.3.2). These logs require conductive drilling mud or ground water with high salinities to work well and, consequently, are not well suited for near-surface investigations in freshwater aquifers. However, normal resistivity logs are widely used to measure variations in water quality.

Induction logs operate on the same principles as surface EM methods that measure conductivity (see Section 6.3.1). Since direct contact with a conductive medium is not required, they are especially useful for logging the dry portion of boreholes where the water table is deep below the surface.

6.4.2 Nuclear Logging Methods

Nuclear logging includes all methods that either detect the presence of radioisotopes or create such isotopes in the vicinity of a borehole. Table 6.4 describes six types of nuclear logs. All types

Table 6.3 Summary of Electrical and EM Borehole Logging Methods in Hydrogeologic Studies

Method	Description	Hydrogeologic Applications
Electric Logs		
Fluid conductivity	A probe that records only the electrical conductivity of the borehole fluids by placing electrodes inside a protective housing	Provides data related to the salinity (concentration of dissolved solids in the borehole fluid); used to locate sources of salt water leaking into artesian wells; aids in interpretation of electric logs
Spontaneous potential (self-potential)	Records the potentials or voltages that develop at the contacts between different lithologies	Widely used in the petroleum industry for determining lithology, bed thickness, and salinity of formation water; generally not applicable for freshwater aquifers
Single-point resistance	Measures the resistance in ohms between an electrode in a well and an electrode at the land surface, or between two electrodes in a well	Excellent for information about changes in lithology; not influenced by bed thickness effects; cannot be used for quantitative interpretation of porosity and salinity
Normal resistivity (short normal, long normal)	Resistance is measured using four electrodes at various spacings on a single probe that is lowered down the hole	Widely used in ground-water hydrology, primarily to determine water quality; quantitative interpretations require corrections for bed thickness, borehole diameter, and other factors
Focused resistivity (guard log, laterolog, dual laterolog)	Uses guard electrodes above and below the current electrode to force the current to flow out into the rocks surrounding the borehole	Designed to measure the resistivity of thin beds or resistive rocks in wells containing conductive fluids; not generally available to water well loggers
Lateral resistivity	Similar to normal resistivity electrode, but electrodes are more widely spaced on the probe	Designed to measure resistivity of rock farther out from the borehole; suitable only for thick beds (>40 ft); marginal for highly resistive rocks
Microresistivity (microlog, contact log, microsurvey, microlateral, micronormal)	Numerous variations; all have short electrode spacing and pads or some kind of contact electrode to decrease the effect of borehole fluid	Designed mainly to determine the presence or absence of mudcake; used primarily by the petroleum industry to determine the resistivity of the 3- to 5-in. zone affected by drilling muds
Induced polarization (IP)	Probe measures response of formation to an injected current; requires water-filled hole	Used to measure clay content and pore fluid chemistry and reactivity
Dipmeter	Includes a variety of wall-contact microresistivity probes; electrodes are on pads located 90 or 120° apart and oriented with respect to magnetic north by a magnetometer in the probe	Probably the best instrument for gathering information on the location and orientation of primary sedimentary structures over a wide variety of hole conditions; provides data on the strike and dip of bedding planes; also on fractures (less precise)
Hole–hole/hole–surface resistivity	Numerous configurations of source and receiver electrodes are possible	Allows three-dimensional modeling of resistivity data to characterize subsurface inhomogeneities
Cross-well AC voltage	A low-frequency alternating current is introduced into the fracture system of two wells and the voltage between the currents and observation wells is measured	Used to characterize the spatial variation in subsurface fracture systems; uncommon method
Electromagnetic Logs		
Induction (dual induction, slimhole EM probe, borehole conductivity meter)	Probe contains two coils: one for transmitting an alternating current into the surrounding rock, and a second for receiving the return signal; measures conductivity	Most instruments require a hole with nonconductive oil-based drilling fluids or air; the recently developed EM39 induction logging tool is suitable for use in freshwater wells

Table 6.3 Summary of Electrical and EM Borehole Logging Methods in Hydrogeologic Studies (Continued)

Method	Description	Hydrogeologic Applications
Microwave sensing (borehole radar, dielectric log)	A variety of methods use microwaves for sensing the subsurface: single and cross-borehole radar (similar to GPR); dielectric log using continuous pulse microwave	Pulsed microwave systems similar to applications for GPR (Section 6.3.5); dielectric log can be used to measure the thickness of hydrocarbons floating on ground water
Nuclear magnetic resonance	Similar to proton precession magnetometer, except response of protons in subsurface water is measured	Measurement of porosity, moisture content, pore-size distribution, available water; near-surface applications most common
Surface-borehole CSAMT	Similar to surface CSAMT (Section 6.3.1), except that borehole sensors are used	Potential for mapping of subsurface conductive zones and three-dimensional characterization of fracture zones in deep boreholes

Note: Boldface = most commonly used methods.

Source: Adapted from Boulding (1993a).

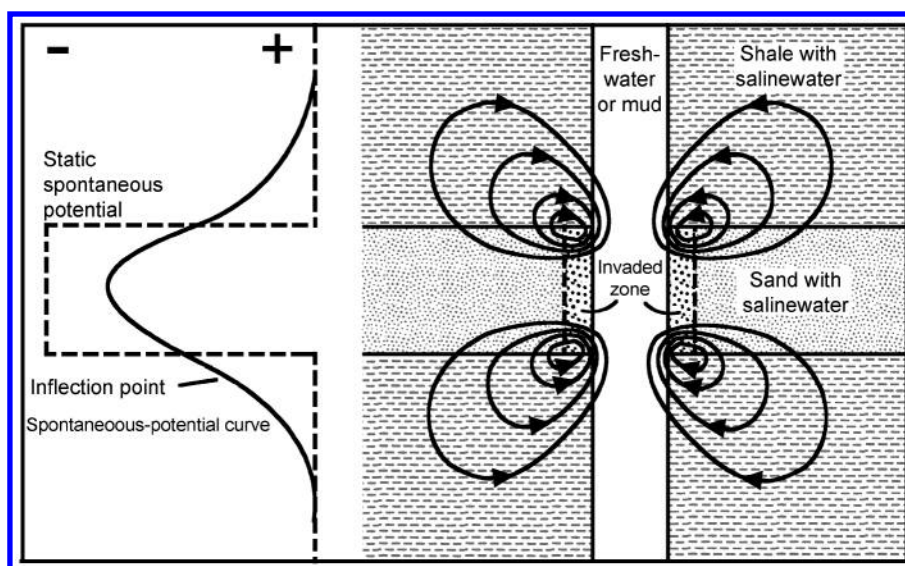


Figure 6.10 The flow of current at typical bed contacts and the resulting spontaneous potential curve (Boulding, 1993b, after Keys, 1990).

are potentially useful in hydrogeologic studies of the vadose and saturated zones because they do not require conductive media, as do most electrical logging methods. Most also allow quantitative interpretation of bulk density, porosity, salinity, and unsaturated moisture content. All of these methods are widely used in the petroleum industry, and neutron logs have been widely used for monitoring of soil moisture content. Gamma and neutron logs are probably the most commonly used in ground-water studies. Gamma spectrometry, gamma-gamma, and neutron activation have been used less frequently and should probably be considered more often.

6.4.3 Acoustic and Seismic Logging Methods

Table 6.5 provides information on three types of acoustic logs and various types of borehole seismic methods. Acoustic logging tools incorporate the signal source and the receiver on the same probe and are used in single boreholes. They are especially valuable for characterizing secondary

Table 6.4 Summary of Nuclear Borehole Logging Methods in Hydrogeologic Studies

Method	Description	Hydrogeologic Applications
Gamma (natural gamma)	Records total natural gamma radiation (primarily from K-40, U-238, and Th-232) from a borehole that is within a selected energy range	The most commonly used nuclear log in ground-water applications; used for identification of lithology (clay and shale particularly) and stratigraphic correlation
Neutron	Probe contains a source of neutrons and detectors that record neutron interactions in the vicinity of the borehole	Widely used to measure saturated porosity and moisture content in the unsaturated zone; can also be used for lithology and stratigraphic correlation
Gamma-gamma (density)	Records the radiation at a detector from a gamma source in the probe after it is attenuated and scattered in the borehole and surrounding rock	Primarily used to determine bulk density, porosity, and moisture content; distinguishes lithologic units; extensively used in the petroleum industry; less frequently used for ground-water applications
Gamma spectrometry (spectral)-, spectro-, spectrometric- gamma)	Records the amount and energy level of gamma photons either on a continuous basis or at selected depths with a stationary probe; types and amounts of radioisotopes can be measured	Allows more precise identification of lithology than gamma log; permits identification of artificial radioisotopes that might be contaminating water supplies; widely used by petroleum industry; should probably be used more frequently in ground-water investigations
Neutron activation (activation, thermal neutron)	Uses neutrons to “activate” stable isotopes in the borehole and identify the activated element by measuring the amount and energy level of emissions (see gamma spectrometry above)	Permits remote identification of elements present in the ground water and adjacent rocks; relatively new technique with potential for wide application in ground-water hydrology
Neutron lifetime (pulsed neutron decay)	Uses a pulsed neutron generator and a synchronously gated neutron detector to measure the rate of decrease of neutron population	Used to measure salinity and porosity; can provide useful data through casing and cement; used by petroleum industry; to date, applications in ground water have been limited

Note: Boldface = most commonly used methods.

Source: Adapted from Boulding (1993a).

porosity and fractures and for assisting in the interpretation of surface seismic survey results. Borehole seismic methods can use various surface-borehole or borehole-borehole source and geophone/hydrophone configurations. They are used primarily for stratigraphic, fracture, and geo-technical characterization.

6.4.4 Lithologic and Hydrogeologic Characterization Logs

Table 6.6 describes seven types of logs that may be useful for characterizing lithology and hydrogeology. *Caliper* logs have numerous variants, but all are intended to measure borehole diameter. They provide essential data for interpreting other types of logs that are affected by variations in borehole diameter and also generate some data on lithology and secondary porosity. Fluid *temperature* can be measured as a gradient (also called thermal resistivity), or changes measured over time at one or more points can be tracked (as when injected water of a different temperature is used as a tracer).

Fluid flow measurements can locate zones of high permeability (fractures and solution porosity) and areas of leakage in artesian wells. The development of thermal and electromagnetic borehole flowmeters that can sense water movement either vertically or horizontally (or both) at very low velocities has greatly enhanced the ability to characterize variations in hydraulic conductivity in boreholes and allows measurement of the direction of ground-water flow in a single well. Borehole

Table 6.5 Summary of Acoustic and Seismic Borehole Logging Methods in Hydrogeologic Studies

Method	Description	Hydrogeologic Applications
Acoustic velocity (sonic, transmit time)	Records the travel time of an acoustic wave from one or more transmitters to receivers in the probe	Useful for providing information on lithology and porosity; limited to consolidated materials in fluid-filled boreholes; beginning to be more widely used in ground-water studies
Acoustic waveform (variable density, three-dimensional velocity, full waveform sonic)	Received acoustic signals are recorded digitally or photographically using oscilloscope displays; the waveforms are analyzed (e.g., amplitude changes, velocity ratios)	Provides information on lithology and structure; various elastic properties can be determined; vertical compressibility of an aquifer can be estimated; fractures can be characterized; not yet widely used in hydrogeologic studies
Acoustic televiewer (seisviewer)	An ATV probe uses a rotating transducer that serves as both transmitter and receiver of high-frequency acoustic pulses; an oscilloscope and light-sensitive paper are used to create a 360° scan of the borehole wall	Provides high-resolution information on the location and character of secondary porosity, such as fractures and solution openings; can also provide the strike and dip of fractures and bedding planes; not yet used extensively in ground-water studies because of cost and complexity
Surface-borehole seismic (vertical seismic profiling/VSP, uphole/downhole)	Various configurations of surface and borehole geophone and seismic source arrays are possible	VSP: Detection of lithologic boundaries, fracture detection, estimation of permeability and hydraulic conductivity Uphole/Downhole: Characterization of geotechnical properties
Crosshole seismic (crosshole shear, crosshole VSP)	Various configurations in which both seismic source and geophones are placed in boreholes	Stratigraphy, porosity, fracture characterization, cavity detection, and measurement of soil dynamic properties
Geophysical diffraction tomography	Tomographic imaging principles applied to seismic data; three configurations are possible for the seismic source: borehole-borehole, surface-borehole, and surface to boreholes	High-resolution possible; can detect isolated inclusions, lithologic boundaries, and homogeneous areas

Note: Boldface = most commonly used methods.

Source: Adapted from Boulding (1993a).

television cameras have the advantage of allowing visual inspection of a borehole for such things as fracture detection and monitoring well integrity.

Borehole *magnetometers* operate on the same principles as surface magnetometers (Section 6.3.4). Magnetometer probes can be especially useful when drilling is required in areas where the presence of buried ferrous metal wastes is suspected. In such situations, lowering the probe to the bottom of the hole approximately every 5 ft may provide advanced warning of the presence of buried drums that are outside the detection limit of surface instruments. Borehole *gravity* is probably the least commonly used borehole method in contaminated site and hydrogeologic applications, but it may have potential value for refining interpretations of data from surface gravity surveys.

Well construction logging is useful for planning cementing operations, installing of casing and screens, performing hydraulic testing, and guiding the interpretation of other logs. The major types of well construction logs are casing logs, for locating cased intervals in wells; cement and gravel pack logs, for locating cement and gravel pack in the annular space outside a casing; and borehole deviation logs, for determining whether a well deviates from the vertical.

6.4.5 Downhole Methods in Ground-Water Contamination Studies

Table 6.7 identifies logging techniques of potential value for specific applications in the following major categories: (1) lithology, stratigraphy, and formation properties; (2) aquifer properties;

Table 6.6 Summary of Miscellaneous Borehole Logging Methods in Hydrogeologic Studies

Method	Description	Hydrogeologic Applications
Caliper	A probe that measures borehole diameter; many types are available: mechanical, electrical, acoustic, and one to four arms	Provides some information on lithology and secondary porosity; essential to guide the interpretation of other types of logs that are affected by borehole diameter
Fluid temperature	Temperature probes are used to record temperature or the rate of change in temperature vs. depth	Widely used in ground-water studies for information on movement of natural or injected water, permeability distribution, and relative hydraulic head
Flowmeters (mechanical/spinner log, thermal, electromagnetic)	Flow measurement with logging probes most commonly is done mechanically with an impeller flowmeter; thermal and EM flowmeters are relatively recent developments that allow more precise readings	Used to measure vertical flow in boreholes, locate intervals of leakage in artesian wells, identify fractures producing and accepting water, and locate zones of high permeability; one of the most useful logging methods available for the study of ground water
Single-borehole tracing	Various methods (injector detector, injection withdrawal, borehole dilution) measure direction and speed of water movement using tracers	Similar to flowmeters (above)
Television/photography	Borehole television and cameras allow visual inspection of borehole both sideways and downward	Information on frequency, size, and orientation of fractures; vertical correlation of rock cores where voids are present; inspection of monitoring well integrity
Magnetic	Probes operating on same principles as surface magnetometers	Changes in lithology; check for buried ferrous metal containers in boreholes before the next depth increment is drilled
Gravity	Microgravity instrumentation designed for borehole use	Complements surface gravity data for structural and stratigraphic interpretation

Note: Boldface = most commonly used methods.

Source: Adapted from Boulding (1993a).

(3) ground-water flow and direction; (4) borehole fluid characterization; (5) contaminant characterization; and (6) borehole/casing characterization.

Downhole logging methods that measure changes in lithology are especially valuable when using drilling methods that do not recover discrete cores at specific intervals. Except where split-spoon samples or diamond rotary cores are taken, this is usually the case (Section 9.2). Downhole logs that measure variations in bulk density, porosity, and fracturing are excellent for identifying heterogeneities in the near-surface ground-water system. Geophysical logs are also useful for identifying zones of high permeability and fracturing for deep-well waste injection. Collier and Alger (1988) and Stegner and Becker (1988) provide overviews of the use of borehole geophysical methods in hydrogeology.¹⁵ More recently, Paillet and Crowder (1996)¹⁶ described a generalized approach for the interpretation of geophysical well logs in ground-water studies.

¹⁵ Collier, H.A. and R.P. Alger. 1988. Recommendations for Obtaining Valid Data from Borehole Geophysical Logs. In: Proceedings of the 2nd National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 897–924.

Stegner, R. and R. Becker. 1988. Borehole Geophysical Methodology: Analysis and Comparison of New Technologies for Ground Water Investigation. In: Proceedings of the 2nd National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 987–1014.

¹⁶ Paillet, F.L. and R.E. Crowder. 1996. A Generalized Approach for the Interpretation of Geophysical Well Logs in Ground-Water Studies: Theory and Application. *Ground Water* 34:883–898.

Table 6.7 Summary of Borehole Log Applications^a

Required Information	Logging Techniques That Might Be Used
Lithology, Stratigraphy, Formation Properties	
General lithology and stratigraphic correlation	Electric (SP, single-point resistance, normal and focused resistivity, dipmeter, IP, cross-well AC voltage); EM (induction, dielectric); all nuclear (open or cased holes); caliper logs made in open holes, borehole television
Bed thickness	Single-point resistance, focused resistivity (thin beds), gamma, gamma-gamma, neutron, acoustic velocity
Cavity detection	Caliper, acoustic televiewer, crosshole radar, crosshole seismic
Sedimentary structure orientation	Dipmeter, borehole television, acoustic televiewer
Large geologic structures	Gravity, surface-borehole/crosshole seismic, crosshole radar
Total porosity/bulk density	Calibrated dielectric, sonic logs in open holes; crosshole radar; calibrated neutron, neutron lifetime, gamma-gamma logs, computer-assisted tomography (CAT) in open or cased holes; nuclear magnetic resonance, induced polarization, crosshole seismic
Effective porosity	Calibrated long-normal and focused resistivity or induction logs
Clay or shale content	Gamma log, induction log, IP log
Relative sand–shale content	Gamma, SP log
Grain size/pore-size distribution	Grain size: Possible relation to formation factor derived from electric, induction, or gamma logs Pore-size distribution: Nuclear magnetic resonance Soil macroporosity: CAT
Compressibility/stress–strain properties	Acoustic waveform, uphole/downhole seismic, crosshole seismic
Geochemistry	Neutron activation log, spectral-gamma log
Aquifer Properties	
Location of water level or saturated zones	Electric, induction, acoustic velocity, temperature or fluid conductivity in open hole or inside casing; neutron or gamma-gamma logs in open hole or outside casing
Moisture content	Calibrated neutron logs, gamma-gamma logs, nuclear magnetic resonance, CAT, dielectric probes
Lithology, Stratigraphy, Formation Properties	
Permeability/hydraulic conductivity	No direct measurement by logging; may be related to porosity, single-borehole tracers methods (injectivity), two-wave sonic amplitude, temperature, nuclear magnetic resonance; estimation may be possible using vertical seismic profiling
Secondary permeability: fractures, solution openings	Caliper, temperature, flowmeters (mechanical, thermal, EM), sonic, acoustic waveform/televiewer, borehole television logs, SP resistance, induction logs, cross-well AC voltage, surface-borehole CSAMT, vertical seismic profiling, crosshole seismic
Specific yield of unconfined aquifers	Calibrated neutron logs during pumping
Ground-Water Flow and Direction	
Infiltration	Temperature logs, time-interval neutron logs under special circumstances or radioactive tracers
Direction, velocity, and path of ground-water flow	Thermal flowmeter; single-well tracer techniques — point dilution and single-well pulse; multiwell tracer techniques
Source and movement of water in a well	Injectivity profile; mechanical, thermal, EM flowmeters; tracer logging during pumping or injection; temperature logs
Borehole Fluid Characterization	
Water quality/salinity	Calibrated fluid conductivity and temperature; SP log, single-point resistance, normal/multielectrode resistivity; neutron lifetime
Water chemistry	Dissolved oxygen, Eh, pH probes; specific ion electrodes
Pore fluid chemistry	Induced polarization log, neutron activation (if matrix effects can be accounted for)
Mudcake detection	Microresistivity, caliper, acoustic televiewer

Table 6.7 Summary of Borehole Log Applications^a (Continued)

Required Information	Logging Techniques That Might Be Used
Contaminant Characterization	
Conductive plumes	Induction log, resistivity, surface-borehole CSAMT
Contaminant chemistry	Specific ion electrodes, fiber-optic chemical sensors
Hydrocarbon detection	Dielectric log, IP log, CPT/laser-induced fluorescence
DNAPLs	Seismic reflection
Radioactive contaminants	Spectral-gamma log
Dispersion, dilution, and movement of waste	Fluid conductivity and temperature logs, gamma logs for some radioactive wastes, fluid sampler
Buried object detection	Geophysical diffraction tomography
Borehole/Casing Characterization	
Well diameter and position of casing, perforations, screens	Gamma-gamma, caliper, collar, and perforation locator, borehole television
Guide to screen setting	All logs providing data on the lithology, water-bearing characteristics, and correlation and thickness of aquifers
Borehole deviation	Deviation log, dipmeter, single-shot probe, dolly and cage tests
Cementing/gravel pack	Caliper, temperature, gamma-gamma; acoustic waveform for cement bond; noise/Sonan log
Casing corrosion/integrity	Borehole television/photography; under some conditions caliper or collar locator
Casing detection/logging	Casing collar locator, borehole television/photography; various electric, nuclear, and acoustic logs
Casing leaks or plugged screen	Tracer and flowmeters
Behind casing flow	Neutron activation and neutron lifetime logs

^a See Table A.2 for additional information on methods that are not specifically identified in the chapter text.
Source: Boulding (1993a).

6.5 CPT AND OTHER DIRECT-PUSH SENSING METHODS

Cone penetration testing (CPT) to measure soil properties has been used since the 1930s in the geotechnical profession. Since the mid-1980s CPT and related instrumentation have been increasingly used in environmental investigations. A typical CPT rig has a thrust capacity of 10 to 20 tons and, depending on soil conditions, can hydraulically advance an instrumented cone in 5-ft increments to depths of 100 ft or more. Large CPT trucks are limited to locations where soils are firm enough to handle the weight of the truck. Tracked CPTs and smaller truck or trailer-mounted direct-push rigs, such as the Geoprobe, can be very mobile. Lunne et al. (1997)¹⁷ is the best single reference for information on cone penetration testing. The focus of the book is on geotechnical applications, but it has a good chapter on geoenvironmental applications.

The standard electronic cone penetration test (ECPT) and piezocone, which also measures pore pressure, allow rapid acquisition of data that can be used for stratigraphic and hydrologic interpretations. CPT and other direct-push rigs can also be used to collect soil cores and ground-water samples, and used to install piezometers and monitoring wells using prepacked screens. A major advantage of CPT/direct-push methods are that they produce minimal drilling wastes when contaminated soils are involved, although care must be taken to grout all direct-push holes in this situation to avoid creating channels for further downward movement of contaminants.

¹⁷ Lunne, T. P.K. Robertson, and J.J.M. Powell. 1997. Cone Penetration Testing in Geotechnical Practice. E&FN Spon, New York.

6.5.1 Standard ECPT and Piezocone

The standard ECPT uses a cone-shaped device instrumented to measure cone resistance (q_c) and sleeve friction (f_s). These parameters, combined with the friction ratio ($R_f = f_s/q_c \times 100$), can be correlated with soil texture for stratigraphic and geotechnical interpretations. The piezocone, also called a CPTU, measures cone resistance and sleeve friction and is also fitted with one or more filters that allow measurement of pore pressure, u . Pore pressure measurements allow detection of the transition from the unsaturated to the saturated zone, and pore pressure dissipation tests can be used to estimate hydraulic conductivity. Although there are a number of soil classification systems that relate ECPT measurements to soil texture, site-specific correlations of one or more ECPT logs with continuous soil cores are necessary when ECPT logs are used primarily for stratigraphic interpretation.

6.5.2 Other CPT and Direct-Push Instrumentation

Numerous types of geophysical and other measurements can be combined with electronic or piezocones, or used with direct-push rigs directly. Electrical resistivity, acoustic, and seismic cones are available. An electrical conductivity cone that does not require a full-size CPT rig has proved very useful as a complementary method for stratigraphic interpretations.¹⁸ Direct observation of the subsurface with CPT video is a promising recent development. The Vis-CPT developed at the University of Michigan allows more detailed stratigraphic interpretations compared to standard ECPT soil classification methods based on both visual description and sophisticated automated image processing techniques.¹⁹ The Geo-VIS, developed as part of the U.S. Navy's Site Characterization Penetrometer System (SCAPS), has proved useful for direct observation of the presences of NAPLs in the subsurface and, with automated image processing techniques, can measure soil porosity, LNAPL concentrations, and residual saturation.²⁰ Singh et al. (1997)²¹ describe CPT dielectric probe for measuring soil moisture content. A fiber-optic-based laser-induced fluorescence (LIF) sensor system can be used to delineate the subsurface presence of petroleum hydrocarbons along with the standard tip resistance and sleeve friction data (ASTM D6187/TA.14).

6.6 SELECTION OF GEOPHYSICAL METHODS

Surface geophysical techniques are most commonly used early in site investigations for preliminary characterization of the geologic and hydrogeologic setting and contaminant plumes. This information serves as a valuable guide for placement of permanent monitoring wells for groundwater sampling and monitoring. The first four major surface geophysical methods identified above are likely candidates for almost any site (ground-penetrating radar will not work where conductivity is high near the surface); metal detection and magnetometry are used whenever the presence of buried drums is suspected and to avoid buried pipelines or tanks when drilling. U.S. EPA's Geophysical Advisor Expert System (Olhoeft, 1992)²² might be useful in determining which of these techniques (plus gravity and radiometric methods) is best suited for specific site and contaminant conditions.

¹⁸ Butler, J.J., Jr., W. McCall, and M.K. Schulmeister. 1999. Hydrostratigraphic Characterization of Unconsolidated Alluvial Deposits with Direct-Push Sensor Technology. Kansas Geological Survey Open File Report 99-40, 13 pp.

¹⁹ Ghalib, A.M., R.D. Hryciw, and E. Susila. 2000. Soil Stratigraphy Delineation by VisCPT. In: Innovations and Applications in Geotechnical Site Characterization (GeoDenver 2000), P.W. Mayne and R. Hryciw (eds.), ASCE Geotechnical Special Publication 97, pp. 65–79.

²⁰ Lieberman, S.H. 2001. Subsurface Soil Analysis Using an *In Situ* Video Imaging System. EPA Tech Trends Issue 43, EPA 542-N-01-004, pp. 1–2.

²¹ Singh, G., B.M. Das, and M.K. Chong. 1997. Measurement of Moisture Content with a Penetrometer. *Geotech. Testing Journal* 20(3):317–323.

²² Olhoeft, G.R. 1992. Geophysics Advisor Expert System, Version 2.0. U.S. Geological Survey Open File Report 92-526, 21 pp. + floppy disk. [Also available from U.S. Environmental Protection Agency Environmental Monitoring Systems Laboratory, P.O. Box 93478, Las Vegas, NV 89193-3478; replaces Version 1.0 [EPA/600/4-89/023], released in 1989; ER, EMI, complex resistivity, SRR, SRL, GPR, GR, radiometric, soil gas]

Remote sensing techniques, other than black-and-white and color photography and, less frequently, color infrared aerial photography, will have limited applications in the study of ground-water contamination, except perhaps where relatively large areas must be investigated. Borehole geophysical methods, however, have potential for use in any studies where subsurface borings are made.

The most basic requirement for successful use of geophysical methods is to select the method that is best at detecting the physical property contrasts of the target (i.e., buried waste, soil bedrock contact, conductive plume, etc.). Greenhouse and Monier-Williams (1985)²³ identified six other considerations in the selection of geophysical methods at contaminated sites: (1) *depth limits of detection and resolution* (see Table A.1); (2) *susceptibility to noise* (electrical, electromagnetic, or vibrations); (3) *corroboration* (confirmation of anomalies by multiple readings or use of more than one method); (4) *ties to borehole sampling* (i.e., confirmation of observations by drilling of monitoring wells for direct observation); (5) *simplicity* (especially important if time-series measurements are to be taken and there is a possibility of multiple contractors taking the measurements); and (6) *cost-effectiveness*. To these considerations might be added: (7) *operator experience* (most geophysical methods require specialized training for use and interpretation of results), and (8) *equipment availability*. For example, many of the less commonly used remote sensing and surface geophysical methods would probably be used more frequently if more contractors knew how to use them or the equipment was more readily available.

Chapter 1 (Remote Sensing and Surface Geophysical Methods) and Chapter 3 (Geophysical Logging of Boreholes) of EPA's *Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide* (Boulding, 1993)²⁴ are recommended for systematic information of potential applications, and comparative advantages and disadvantages of different geophysical methods. A companion document, *Use of Airborne, Surface, and Borehole Geophysical Techniques at Contaminated Sites* (Boulding, 1993),²⁵ is recommended as a source for journal and conference paper citations that provide examples of specific applications of one or more geophysical methods of interest.

Most geophysical techniques require highly trained and experienced personnel for data collection and interpretation. When dealing with geophysical contractors, there should be a clear understanding about the services being performed. Many geophysical contractors just provide the raw geophysical data as their standard service and charge extra for interpretation of data.

6.7 GUIDE TO MAJOR REFERENCES

[Table 6.8](#) provides an index to major references on remote sensing, general geophysics, and specific surface geophysical methods, and [Table 6.9](#) provides an index to major references on borehole geophysics.

6.7.1 General Geophysics

Historically, geophysical field methods have been primarily the domain of petroleum and mineral exploration geologists, and textbooks written from this perspective remain an important source of information on basic theory and application of geophysical methods in the study of contaminated sites. Many of the references indexed in Table 6.8 include annotations of methods covered by individual texts (abbreviations in these annotations are defined at the end of the table). Older texts can provide useful information on basic principles, and even newer texts can become

²³ Greenhouse, J.P. and M. Monier-Williams. 1985. Geophysical Monitoring of Ground Water Contamination around Waste Disposal Sites. *Ground Water Monitoring Review* 5(4):63–69.

²⁴ Boulding, J.R. 1993. *Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide*, Vol. I, Solids and Ground Water. EPA/625/R-93/003a. Available from CERL.

²⁵ Boulding, J.R. 1993. *Use of Airborne, Surface, and Borehole Geophysical Techniques at Contaminated Sites: A Reference Guide*. EPA/625/R-92/007. Available from CERL.

rapidly outdated with respect to specific methods. Information on the latest developments in geophysical methods is most likely to appear in the exploration-oriented geophysical journals: *Geophysics*, *Geophysical Prospecting*, and *Geoexploration* (renamed *Journal of Applied Geophysics* in 1992). The expanded abstracts of the annual meeting of the Society of Exploration Geophysicists (SEG) is another important source of information on recent developments in geophysical methods. The periodic International Conferences on Ground Penetrating Radar are a good source of information of developments and applications of GPR. The 8th International GPR Conference was held at the University of Queensland in 2000.

6.7.2 Ground Water and Contaminated Sites

Zohdy et al. (1974), although a relatively old document, is still the best single report covering applications for surface geophysical methods to ground-water investigations. Haeni (1988) is a basic reference on use of seismic refraction in ground-water investigations. Benson et al. (1984) is a good reference for more detailed information on applications of commonly used surface geophysical methods at contaminated sites. Keys and MacCary (1971) and Keys (1990, 1997) are good basic references on hydrogeologic applications of borehole geophysical methods.

Information on the latest developments in application of geophysical methods in the investigation of ground-water and contaminated sites is most likely to appear in the hydrogeologic journals *Ground Water* and *Ground Water Monitoring Review* (renamed *Ground Water Monitoring and Remediation* in 1993). Other important journals include *Water Resources Research* and *Journal of Hydrology*.

The Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP), sponsored by the Society of Engineering and Mineral Exploration Geophysicists (SEMEG), has been held annually since 1988 and is an exceptional source of information on hydrogeologic and contaminated site applications. Each volume of proceedings includes several applications-oriented review papers and numerous case studies. In 1992, SEMEG became the Environmental and Engineering Geophysical Society (EEGS), which continues to sponsor the SAGEEP.

Another important source of information on recent developments is a number of symposium series sponsored by the National Water Well Association (NWWA) or the affiliated Association of Ground Water Scientists and Engineers (AGWSE). NWWA changed its name to the National Ground Water Association (NGWA) in 1992. Table 5.12 lists the year and title of a number of these conference and symposium series. Proceedings of the NWWA's annual National Outdoor Action Conference (NOAC) on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods (titled National Symposium on Aquifer Restoration and Ground Water Monitoring prior to 1987) generally provide the largest number of papers related to geophysical methods. The NOAC conference series was discontinued in 1997. The NGWA regional ground-water issues conferences typically have at least six papers related to use of geophysical methods.

The annual Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, which continues to be sponsored jointly by NGWA and the American Petroleum Institute, is an important source for papers on developments in the use of geophysical methods for detection of hydrocarbons.

6.7.3 Evaluation of Literature References

The field of geophysics in general and specific applications in ground-water and contaminated site investigations is changing so rapidly that great care is required when evaluating the literature, especially when dealing with a method that is outside one's area of expertise. Several factors affect the weight that should be given to conclusions or recommendations concerning a particular method: (1) whether it is from a peer-reviewed or non-peer-reviewed source; (2) where the authors come from; and (3) how recently it has been published.

Greatest weight should be given to the content of papers published in peer-reviewed scientific journals such as *Geophysics*, *Ground Water*, and *Ground Water Monitoring Review*. Most conference proceedings (American Society for Testing and Materials conferences being an exception) are not peer reviewed; consequently, there is more likely to be diversity of opinion concerning conclusions or recommendations in individual papers. When non-peer-reviewed papers are considered, greater weight can be given to those authored by individuals from academic institutions or research-oriented government agencies (e.g., U.S. Geological Survey, personnel from EPA research laboratories) than to papers authored by consultants who may have an interest in promoting a particular method. Finally, more recently published papers can generally be given greater weight than earlier publications because they are more likely to address recent developments and advances in geophysical techniques. As a general rule, review of multiple references from a variety of sources that deal with a specific method should help determine the method's appropriateness for a specific application or for site-specific conditions. When in doubt, one or more experts should be consulted.

Table 6.8 Index to Major References on Remote Sensing and Surface Geophysical Methods

Topic	Reference
Remote Sensing	
General	Colwell (1983), Congalton and Green (1998), Cracknell and Hayes (1991), Dury (1990), Foody and Curran (1993), Hoffman and Markman (2001), Holz (1973), Iliffe (2000), Johnson and Pettersson (1987), Kondratyev (1969), Rees (1990), Reeves (1968, 1975), Regan (1980), Sabins (1978), Ulaby et al. (1982 — microwave), Watson and Regan (1983); <u>Hydrology/Geology/Contamination Applications</u> : Boulding (1993a, 1993b), Burgy and Algaz (1974), Deutsch et al. (1979), Drury (1987), Ellyett and Pratt (1975), Goodison (1985), Kelly and Mares (1993), Kuehn et al. (2000), Lund (1978), Reeves (1968), Scherz (1971), Scherz and Stevens (1970), Sers (1971), Singhroy et al. (1996), Thomson et al. (1973)
Aerial Photography	Avery (1968), Ciciarelli (1991), Denny et al. (1968), Drury (1987), Falkner (1994), Falkner and Morgan (2001), Johnson and Gnaedinger (1964 — bibliography), Lattman and Ray (1965), Lueder (1959), Miller and Miller (1961), Ray (1960), SCS (1973), Strandberg (1967), Way (1973), Wolfe (1974 — photogrammetry), Wright (1982)
Airborne Geophysics	<u>AEM</u> : Palacky (1986), Palacky and West (1991), Smith et al. (1989); <u>Aeromag</u> : Smith et al. (1989)
General Geophysics	
General Texts ^a	Beck (1981), d'Arnaud Gerkins (1989), Dobrin and Savit (1988), Eve and Keys (1954), Garland (1989), Grant and West (1965), Griffiths and King (1981), Hansen et al. (1967), Heiland (1940), Howell (1959), Jakosky (1950), Kearey and Brooks (1991), Liboutry (2000), Milsom (1996), Nettleton (1940), Parasnis (1975, 1979), Reynolds (1997), Robinson and Coruh (1988), Sharma (1986, 1998), Sheriff (1989), Straugh et al. (2001), Telford et al. (1990), Valley (1965), Van Blaricom (1980), Ward (1990a); <u>Glossaries</u> : Sheriff (1968, 1991); <u>Engineering</u> : McCann (1998), Paillet and Saunders (1990), SEG (various dates), SEMEG (1988 — present), U.S. Army Corps of Engineers (1979), Ward (1990c); <u>Nondestructive Testing Methods</u> : ASTM (annual), Lord and Koerner (1987), McGonnagle (1961), Sharp (1970)
Ground Water	Erdélyi and Gálfi (1988), Morely (1970), NWWA (1984, 1985, 1986), Redwine et al. (1985), Rehm et al. (1985), Taylor (1984), U.S. Geological Survey (1980), Violette (1987), Ward (1990b), Zohdy et al. (1974); <u>Bibliographies</u> : Handman (1983), Johnson and Gnaedinger (1964), Lewis and Haeni (1987), Rehm et al. (1985), van der Leeden (1991); <u>USGS Toolbox Approach for Fractured Rock</u> : See Table 7.6
Contaminated Sites	Aller (1984), API (1991), Benson et al. (1984), Boulding (1993a, 1993b), Costello (1980), EC&T et al. (1990), Frischknecht et al. (1983), HRB-Singer (1971), Lord and Koerner (1987), NWWA (1984, 1985, 1986), O'Brien & Gere (1988), Olhoeft (1992), Pitchford et al. (1988), SEMEG (1988 — present), Technos (1992), U.S. EPA (1987, 1999 — DNAPLs), Van Eeckhout and Calef (1992), Waller and Davis (1984), Ward (1990b); <u>Review Papers</u> : Benson (1991), Evans and Schweitzer (1984), Hoekstra and Hoekstra (1990)
Specific Surface Geophysical Methods	
Electrical Resistivity	<u>Texts</u> : Bhattacharya and Patra (1968), Goldman (1990 — nonconventional methods), Keller and Frischknecht (1970), Kofoed (1979), Kunetz (1966), Mooney (1980), Patra and Mallick (1980), Roux (1978), Soiltest, (1968); <u>Interpretation</u> : Kalenov (1957), Mooney and Wetzell (1956), Orellana and Mooney (1966, 1972), Van Nostrand and Cook (1966), Verma (1980); <u>Geoelectric Properties</u> : Parkhomenko (1967), Wheatcraft et al. (1984)
Induced Polarization	Baizer and Lund (1983), Bertin and Loeb (1976), Botcher (1952), Fink et al. (1990), Sumner (1976), Wait (1959, 1982), Wheatcraft et al. (1984)
Electromagnetics	<u>Basic Theory</u> : Jackson (1975), Kong (1975), Nabighian (1988), Stratton (1941), Wait (1985); <u>EM Wave Behavior</u> : Chew (1990), Jordon (1963), Kong (1975), Lorrain and Carson (1970), Schelnukoff (1943), Wait (1970, 1981, 1985), Ward and Morrison (1971)

Table 6.8 Index to Major References on Remote Sensing and Surface Geophysical Methods (Continued)

Topic	Reference
EM Field Methods	<u>EMI</u> : Hoyt (1974), Kaufman and Keller (1983), Kraus (1984), Nabighian (1988, 1991), Rokityanski (1982), Verma (1982 — three-layer interpretation data), Wait (1971, 1982); <u>IDEM</u> : Felsen (1976), Goldman (1990), Kaufman and Keller (1983), Nabighian and Macnae (1991); <u>Magnetotellurics</u> : Kaufman and Keller (1981), Porstendorfer (1975), Vozoff (1986, 1991); <u>VLF</u> : McNeill and Labson (1991); <u>CSAMT</u> : Zonge and Hughes (1991)
Ground-Penetrating Radar	Hänninen and Autio (1992), Lucius et al. (1990), Olhoeft (1988 — bibliography), Pilon (1992), Pittman et al. (1984), Rossiter and Bazely (1980), SCS (1988), Sneddon et al. (2000), Ulriksen (1982); <u>Subsurface Dielectric Properties</u> : Akhadow (1980), Daniel (1967), Hasted (1974), Kracchman (1970), Tareev (1975), van Beek (1965), von Hippel (1954a, 1954b)
Seismic Refraction	<u>Texts</u> : Badley (1985), Dix (1952 — oil prospecting), Haeni (1988 — hydrogeology), Mooney (1984), Musgrave (1967), Palmer (1986), Redpath (1973), Waters (1981); <u>Analysis/Interpretation</u> : Berkhout (1985, 1988), Fagin (1991), Palmer (1980), Russell (1988), Slotnick (1959), Tucker (1982), Tucker and Yorsten (1973); <u>Wave Theory Texts</u> : Auld (1990), Berkhout (1987), Bland (1988), Davis (1988), White (1965); <u>Rock Properties</u> : Carmichael (1982), Mayo et al. (1998)
Continuous Seismic Profiling	<u>Texts</u> : Burdic (1991), Coates (1989), EG&G Environmental Equipment Division (1977), Hassab (1989 — signal processing), Sylwester (1983), Trabant (1984); <u>Interpretation</u> : Badley (1985), Leenhart (1969), Roksandic (1978), Sangree and Widmier (1979), Tufekci (1978)
Other Seismic	Lynn and McBeth (2000 — seismic anisotropy), Sato and Fehler (1997); <u>Seismic Reflection</u> : Badley (1985), Danbom and Domenico (1987), Graebner et al. (2001 — three-dimensional), Kleyn (1983), Steeples and Miller (1988), Waters (1981); <u>Seismic Shear</u> : Danbom and Domenico (1987), Dohr (1985), Ensley (1987 — bibliography); <u>Acoustic Emission Monitoring</u> : U.S. EPA (1979), Waller and Davis (1984); <u>Sonar</u> : Saucier (1970)
Magnetometry	Bozorth (1951), Breiner (1973), Chikazumi (1964), Hinze (1988), Lahee (1961), Nettleton (1971, 1976)
Gravity	Hinze (1988), Lahee (1961), Nettleton (1971, 1976), Zohdy et al. (1974)
Geothermal Methods	<u>Texts</u> : Brown et al. (1983), Eve and Keys (1954), Gougel (1976), Howell (1959), Jessup (1990), Rehm et al. (1985), Sharma (1986), Sheriff (1989), Stevens et al. (1975), Summers (1971 — bibliography); <u>Soil Thermal Properties</u> : Carlslaw (1986), Farouki (1981), Kersten (1949), Lee (1965), Wechsler et al. (1965)

Note: See method abbreviations at end of Table 6.8 references.

^a Most texts on geophysics cover electrical, electromagnetic, seismic, magnetic, and gravity methods. Check annotations for major topics covered by texts identified at the beginning of the table.

Table 6.8 References (Appendix F contains references for figure and table sources.)

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* See Preface for information on how to obtain documents from CERI and NTIS.

Method Abbreviations: AEM = airborne electromagnetic; AFMAG = audiofrequency magnetic; AMT = audio-magnetotelluric; ATV = acoustic televiewer; BH = borehole; CSAMT = controlled source audiomagnetotelluric; CSP = continuous seismic profiling; EM = electromagnetic (used when not enough information is available to classify further); EMI = electromagnetic induction; ER = electrical resistivity; GDT = geophysical diffraction tomography; GPR = ground-penetrating radar; GR = gravity; GT = geothermal; IP/CP = induced polarization/complex resistivity; IR = infrared; MAG = magnetic; MD = metal detection; MT = magnetotelluric; S = seismic (used when not enough information is available to classify further); SASW = spectral analysis of surface waves; SLAR = side-looking airborne radar; SP = self-potential (surface and borehole), SRL = seismic reflection; SRR = seismic refraction; TC = telluric current; TDEM = time domain electromagnetic; VLF = very low frequency; VSP = vertical seismic profiling.

Table 6.9 Index to Major References on Borehole Geophysics

Topic	References
Bibliographies	Johnson and Gnaedinger (1964), Prensky (various dates), Rehm et al. (1985), Taylor and Dey (1985), van der Leeden (1991)
Glossary	Society of Professional Well Log Analysts (1975)
General Texts/Reports	
Log Method Texts	Dresser Atlas (1974, 1982), Ellis (1987), Guyod and Shane (1969), Hallenberg (1983), Hamilton and Myung (1979), Hearst and Nelson (1985), Hearst et al. (2000), Helander (1983), Kelly (1969), Labo (1987), LeRoy et al. (1987), Lynch (1962), Nelson (1985), Scott and Tibbets (1974), Serra (1984a), Telford et al. (1990), Tittman (1986)
Log Interpretation	Asquith and Gibson (1982), Birdwell Division (1973), Doveton (1986), Dresser Atlas (1975, 1979, 1982), Emerson and Webster (1970), Foster and Beaumont (1990), Hallenberg (1984, 1997a, 1997b), Hilchie (1982a, 1982b), Pirson (1963, 1983), Rider (1986, 1996), Schlumberger (1972, 1974, 1989a, 1989b, 1991), Serra (1984b), Tearpock and Bischke (1991), Wyllie (1963)
Imaging/Tomography	<u>Borehole Imaging</u> : Lines and Scales (1987), SPWLA (1990 — borehole imaging); <u>Tomography</u> : Davis (1989), Desaubies et al. (1990), Lines and Scales (1987), Mahannah et al. (1988), Stewart (1991), Tweeton (1988)
Log Quality Control	Bateman (1985), Theys (1991)
Borehole Logging Symposia	Canadian Well Logging Society (various dates), Killeen (1985), Minerals and Geotechnical Logging Society (1985–2002), NWWA (1984, 1985, 1986), SPWLA (1960–present)
Specific Logging Methods	
Electrical and EM	<u>Electrical</u> : Guyod (1952, 1957, 1958, 1965), Guyod and Pranglin (1959), Hilchie (1979), Keller and Frischknecht (1970), Patra and Nath (1999), Patten and Bennett (1963), Ross and Ward (1984); <u>Focused Resistivity</u> : Moran and Chemali (1985), Roy (1982); <u>EM Induction</u> : Kaufman and Keller (1989), McNeill (1986), McNeill et al. (1990); <u>Dielectric</u> : Keech (1988); <u>NMR</u> : Abragam (1961), Jackson (1984), Morrison (1983), Schlichter (1963); <u>Dipmeter</u> : Bigelow (1985); <u>Crosshole Resistivity</u> : Daily and Owen (1991), Daniels (1983); <u>Borehole CSAMT</u> : West and Ward (1988)
Nuclear Logging	IAEA (1968, 1971), SPWLA (1978a); <u>Neutron</u> : Beck (1981), Bell (1973), Greacen (1981), Institute of Hydrology (1981), IAEA (1970), Johnson (1962), Morrison (1983), Olgaard (1965), SPWLA (1978a), Thompson et al. (1989), Tittle (1961), Weinberg and Wignor (1958); <u>Gamma</u> : Guyod (1965), Killeen (1982), Patton and Bennett (1963), SPWLA (1978a); <u>Gamma-Gamma</u> : Morrison (1983), SPWLA (1978a), Thompson et al. (1989); <u>Gamma Spectrometry</u> : Adams and Gasparini (1970), Schneider (1982); <u>Neutron Activation</u> : Schneider (1982); <u>Protection</u> : Blizard (1958), U.S. Nuclear Regulatory Commission (1985)
Acoustic/Seismic	<u>Acoustic</u> : Guyod and Shane (1979), Paillet and Cheng (1991), SPWLA (1978b); <u>Crosshole</u> : Butler and Curro (1981); <u>VSP</u> : Balch and Lee (1984), CH2M Hill (1991), Gal'perin (1974), Hardage (1985, 2000), Toksoz and Stewart (1984); <u>Seismic Tomography</u> : Mahannah et al. (1988), Stewart (1991)
Miscellaneous	<u>Gravity</u> : Hearst and Carlson (1982), Robbins (1986); <u>Flowmeters</u> : Molz et al. (1990), Taylor et al. (1990), Wheatcraft et al. (1986), Young and Pearson (1990); <u>Borehole Television</u> : Morahan and Dorrier (1984); <u>Temperature</u> : Stevens et al. (1975); <u>Fluid Conductivity</u> : Tellam (1992)
Applications	
Ground Water	Bennett and Patten (1960), Emerson and Webster (1970), Hodges and Teasdale (1991), IAEA (1971), Johnson (1968), Jorgenson (1989), Keys (1990, 1997), Keys and MacCary (1971), Paillet and Crowder (1996), Patten and Bennett (1963), Respolo (1989), Taylor and Dey (1985), Welenco (1994); <u>Other Texts with Sections on Borehole Geophysics</u> : Beesley (1986), Brown et al. (1983), Bureau of Reclamation (1981), Campbell and Lehr (1973), Davis and DeWiest (1966), Driscoll (1986), Everett (1985), Redwine et al. (1985), Rehm et al. (1985), U.S. Army Corps of Engineers (1979)

Table 6.9 Index to Major References on Borehole Geophysics (Continued)

Topic	References
Other Applications	<u>Contaminated Sites</u> : Adams et al. (1983), Benson (1991), Boulding (1993a, 1993b), Keys (1997), Stowell (1989), Taylor et al. (1990), Technos (1992), U.S. EPA (1987), Wheatcraft et al. (1986); <u>Fracture/Flow Characterization</u> : Nelson (1985), Robbins and Hayden (1988), Ross and Ward (1984), Serra (1984b), Taylor (1989), Tellam (1992), West and Ward (1988), Williams and Conger (1990), Young and Pearson (1990), see also USGS Toolbox Approach Table 7.6; <u>Well Construction/Integrity</u> : Gearhart Industries (1982), Nielsen and Aller (1984), Thornhill and Benefield (1990), Yearsley et al. (1991)

Table 6.9 References (Appendix F contains references for figure and table sources.)

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- Yearsley, E.N., R.E. Crowder, and L.A. Irons. 1991. Monitoring Well Completion Evaluation with Borehole Geophysical Density Logging. *Ground Water Monitoring Review* 11(1):103–118. [Acoustic cement bond, gamma-gamma]
- Young, S.C. and J.S. Pearson. 1990. Characterization of Three-Dimensional Hydraulic Conductivity Field with an Electromagnetic Borehole Flowmeter. In: *Proceedings of the Fourth National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, Ground Water Management* 2:83–97.

* See Preface for information on how to obtain documents from CERI and NTIS.

CHAPTER 7

Characterization of Vadose Zone and Ground Water Hydrology

Many methods are available for characterizing vadose zone and ground-water hydrology. A single chapter can only provide an overview of major techniques and identify key considerations when performing hydrogeologic mapping. The U.S. EPA's guide to *Subsurface Characterization and Monitoring Techniques* (Boulding, 1993/T7.5) is recommended for use as a companion to this chapter. This two-volume document is available at no cost from the U.S. EPA's Center for Environmental Research information (see Preface for ordering information). Appendix A in this handbook contains major method summary tables from that guide, which can be used to quickly identify the location of specific methods of interest. Appendix B provides an index and listing of American Society for Testing and Materials (ASTM) standards related to subsurface hydrologic characterization.

7.1 MEASUREMENT OF VADOSE ZONE HYDROLOGIC PARAMETERS

Historically, measurement of vadose zone hydrologic parameters has been the domain of soil physicists and agronomists because of their significance for plant growth, and engineers because water content of soil materials significantly affects engineering behavior. The U.S. Environmental Protection Agency's increasing emphasis on vadose zone monitoring as an early-warning system for ground-water protection means that familiarity with methods for measuring vadose hydrologic characteristics is necessary for environmental professionals dealing with soil and ground-water protection or remediation. This section addresses the following aspects of vadose zone hydrology: (1) measurement of matric potential and moisture content (Section 7.1.1), (2) measurement of infiltration and hydraulic conductivity, (3) measurement of other water budget parameters, and (4) miscellaneous hydrologic parameters and measurement/estimation of vadose zone water flux.

7.1.1 Matric Potential and Moisture Content

Water state in the vadose zone is measured in terms of *positive pressure head* when the soil is saturated and *negative pressure potential* or *suction* when the soil is unsaturated (Section 2.4.1). Table A.3 provides summary information on six major techniques for measuring soil water potential and a dozen methods for measuring soil moisture content. The measurement of soil water potential and moisture content in the vadose zone is intimately connected, and a specific measurement technique can be classified as measuring potential or moisture content, depending on the perspective of the writer in the literature. Either measurement can be used to obtain the other if a *moisture characteristic curve*, a plot of the relationship between moisture content and suction, has been

developed. *Porous cup tensiometers* are the most commonly used method for measuring soil water potential in the vadose zone. Recent design improvements for porous cup tensiometers have extended their operational depth range from around 7 to 150 m.¹ The *gravimetric* method is most commonly used to measure moisture content from soil samples, and the *neutron probe* and *gamma-gamma* methods are most commonly used for *in situ* measurement of soil moisture. The relatively recent commercial availability of *dielectric* or *capacitance* sensors is likely to increase the use of this method, which provides accuracy similar to that of the neutron probe, without some of the disadvantages of nuclear methods (i.e., radioactive sources). Similarly, *time domain reflectometry* (TDR), a relatively new method, is becoming more widely used with the advent of commercially available units. TDR systems are more expensive than dielectric probes. O'Brien and Oberbauer (2001)² give information on how to construct an inexpensive portable dielectric probe system that costs about half the amount of commercial units. *Thermo-time domain reflectometry* is a new development that combines TDR with heat pulse sensors to permit simultaneous measurement of soil water content, electrical conductivity, thermal diffusivity, and volumetric heat capacity.³ Ren et al. (2000) used thermo-TDR to measure soil water flux and pore water velocity, and Ochsner et al. (2001) used it to simultaneously measure water content, air-filled porosity, and bulk density.⁴ Another area of active research is the use of fiber-optic sensors for measuring soil water content.⁵ All methods for vadose zone measurement of water content or matric potential have limitations with respect to soils contaminated with nonaqueous phase liquids, due to interference effects.

7.1.2 Infiltration and Hydraulic Conductivity

Characterization of water movement in the vadose zone is complicated by the fact that hydraulic conductivity varies as a function of pressure potential and moisture content. Various terms are used to describe hydraulic conductivity in the vadose zone:

1. *Saturated hydraulic conductivity* (K_{sat}), which is the hydraulic conductivity at saturation with no entrapped air. This state rarely is achieved in the vadose zone, except perhaps in the zone of seasonal fluctuation of an unconfined water table.
2. *Field-saturated hydraulic conductivity* (K_{fs}), also called the *satiated* hydraulic conductivity, which is the hydraulic conductivity when entrapped air is present; it can be as much as 50% below the true K_{sat} (Reynolds and Elrick, 1986).⁶ Methods for measuring saturated hydraulic conductivity above the water table usually measure K_{fs} . Another term, $K_{(sat)}$, has been proposed by Bouma (1982)⁷ for hydraulic conductivity measurements of the soil matrix without macropore flow (Figure 7.1c). $K_{(sat)}$ will be less than K_{sat} or K_{fs} because water flows more rapidly in macropores than in the soil matrix. The term K_{sat} often is loosely used for reporting measurements that should more accurately be termed K_{fs} .
3. *Unsaturated hydraulic conductivity* (K_{unsat}), which is the hydraulic conductivity of soil at negative pressure potentials. $K(\phi)$ is the term usually used to describe the hydraulic conductivity-pressure

¹ Jones, J.B. 2001. Advanced Tensiometers for Vadose Zone Monitoring. EPA Tech Trends 43, EPA 542-N-01-004, pp. 2–3.

² O'Brien, J.J. and S.F. Oberbauer. 2001. An Inexpensive Portable Meter for Measuring Soil Moisture. Soil Sci. Soc. Am. J. 65:1081–1083.

³ Ren, T., K. Noborio, and R. Horton. 1999. Measuring Soil Water Content, Electrical Conductivity, and Thermal Properties with a Thermo-Time Domain Reflectometry Probe. Soil Science Society of America Journal 63:450–457.

⁴ Ren, T., G.J. Kluitenberg, and R. Horton. 2000. Determining Soil Water Flux and Pore Water Velocity by a Heat Pulse Technique. Soil Science Society of America Journal 64:552–560.

Ochsner, T.E., R. Horton, and T. Ren. 2001. Simultaneous Water Content, Air-Filled Porosity, and Bulk Density Measurements with Thermo-Time Domain Reflectometry. Soil Science Society of America Journal 65:1618–1622.

⁵ Garrido, F., M. Ghodrati, and M. Chendorain. 1999. Small-Scale Measurement of Soil Water Content Using a Fiber Optic Sensor. Soil Science Society of America Journal 63:1505–1512.

⁶ Reynolds, W.D. and D.E. Elrick. 1986. A Method for Simultaneous *In Situ* Measurement in the Vadose Zone of Field Saturated Hydraulic Conductivity, Sorptivity and the Conductivity-Pressure Head Relationship. Ground Water Monitoring Review 6(4):84–95.

⁷ Bouma, J. 1982. Measuring the Hydraulic Conductivity of Soil Horizons with Continuous Macropores. Soil Science Society of America Journal 46:438–441.

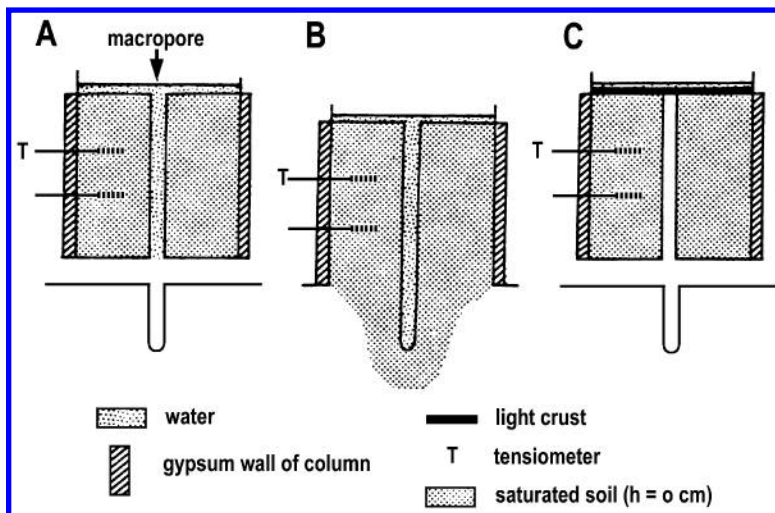


Figure 7.1 Schematic representation of three types of flux measurements using the column-crust method (Boulding, 1993b, after Bouma, 1982).

potential function, and $K(\theta)$ describes the hydraulic conductivity-moisture content function. Complete characterization of K_{unsat} requires measuring hydraulic conductivity at a range of moisture contents to develop a $K(\theta)$ curve or at a range of pressures to develop a $K(\phi)$ curve. $K(\phi)$ curves for two different soil materials are illustrated in Figure 2.9. These functions are subject to *hysteresis* (i.e., K_{unsat} can differ at the same water content or matric potential, depending on whether the soil is wetting or drying).

Infiltration. The infiltration capacity of a soil is a critical element of water budget calculations because it affects how much precipitation that reaches the ground surface enters the soil and how much moves off a site as surface runoff. The infiltration rate generally is the same as the unsaturated and saturated hydraulic conductivity, except that some processes, such as the initial moisture content (see Figure 7.2), crusting, or sediment clogging, might cause different infiltrations at the ground surface compared to the subsurface, with all other soil factors being equal. Table A.4 summarizes information on eight methods for measuring or estimating infiltration. These methods can be grouped into four general categories: (1) *impoundment* methods, where infiltration is below a water surface (seepage meters, instantaneous rate, and impoundment water budget); (2) *land surface* methods (cylinder infiltrometers, infiltration test basins, and sprinkler infiltrometers); (3) *watershed* methods for estimating infiltration over larger areas (watershed average and empirical relations); and (4) *infiltration equations*. Often infiltration can be estimated using empirical relations or infiltration equations using other variables, which can be obtained with instruments for measuring saturated and unsaturated hydraulic conductivity (see below).

Measurement of Unsaturated Hydraulic Conductivity. Table A.4 summarizes information on nine methods for measuring or estimating unsaturated hydraulic conductivity from field measurements. Most of these methods can be used to develop $K(\phi)$ or $K(\theta)$ relationships, which once established allow subsequent monitoring to focus on changes in either pressure potential or moisture content. The *instantaneous profile method* is the most commonly used method for accurate measurement of unsaturated hydraulic conductivity in the field. Various *draining profile* methods are simpler and less expensive to use if the simplifying assumptions apply to the site of interest. Another common procedure is to collect undisturbed core samples and measure K_{unsat} in the laboratory (Klute and Dirksen, 1986).⁸ ASTM D5126 (Table A.14) provides guidance on selecting field

⁸ Klute, A. and C. Dirksen. 1986. Hydraulic Conductivity and Diffusivity: Laboratory Methods. In: *Methods of Soil Analysis*, 2nd ed., Part 1, A. Klute (ed.), Agronomy Monograph 9, American Society of Agronomy, Madison, WI, pp. 687–734.

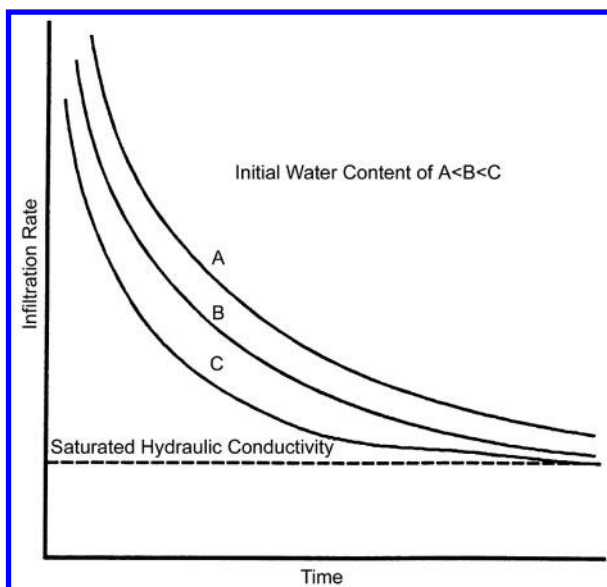


Figure 7.2 The effect of initial water content of soil on infiltration rates (Everett et al., 1983).

methods for measuring unsaturated hydraulic conductivity in the vadose zone. One difficulty in determining unsaturated hydraulic properties in relatively impermeable materials and materials at very low water content is that long periods of time are required to attain steady-state conditions. The steady-state centrifugation method (SSCM) is a new technique that substantially reduces the time required for testing such materials (ASTM D6527/TA.14).

Measurement of Saturated Hydraulic Conductivity. Table A.4 summarizes information on 10 methods for measuring K_{fs} above a shallow water table and 5 methods for measuring K_{fs} above a deep water table. The *cylinder* or *ring* infiltrometer is a widely used method that measures both infiltration and K_{fs} at the soil surface. Most other shallow methods require a borehole and devices at the surface to control the flow of water into the hole to achieve steady-state infiltration before measurements are taken. The *constant-head borehole infiltration* or *shallow-well pump-in* method and the *Guelph permeameter* probably are the most commonly used methods for measuring K_{fs} . Most of these methods are restricted to a depth of 2 m or less, but the recently developed *compact constant-head permeameter* can be used to depths of 10 m. Most methods for measuring K_{fs} above a deep water table require drilling or relatively large-diameter boreholes (at least 6 in.) and a large supply of water, which can be pumped into the borehole. ASTM D5126 (Table A.14) provides guidance on selecting field methods for measuring saturated hydraulic conductivity in the vadose zone. Recently, a *restricted interval Guelph (RIG) permeameter* has been developed that can be used in small-diameter boreholes of any orientation. Friefeld and Oldenburg (2000)⁹ describe use of the RIG permeameter in welded tuffs at Yucca Mountain, NV. *Tension infiltrometers* are widely used to measure soil hydraulic properties near saturation in the field. Zhang et al. (1999)¹⁰ describe refinement to this technique for measuring saturated and nearly saturated hydraulic conductivities in the field.

7.1.3 Other Vadose Water Budget Parameters

Water movement and transport of contaminants in the vadose zone is determined by the amount of precipitation that enters the ground by infiltration, and the amount of water that is removed from

⁹ Friefeld, B.M. and C.M. Oldenburg. 2000. Restricted Interval Guelph Permeameter: Theory and Application. Water Resources Res. 36:1373–1380.

¹⁰ Zhang, Y., R.E. Smith, G.L. Butters, and G.E. Cardon. 1999. Analysis and Testing of a Concentric-Disk Tension Infiltrometer. Soil Sci. Soc. Am. J. 63:544–553.

the soil by evaporation from bare soil or by evapotranspiration where vegetation covers the soil. Table A.5 provides information on techniques for measuring or estimating (1) hydrometeorological parameters, and (2) evaporation and evapotranspiration for water budget calculations in the vadose zone and shallow ground-water systems. Methods for measuring and estimating infiltration are covered in the previous section.

Hydrometeorological Data. Table A.5 provides some general summary information on 38 techniques for measuring six major hydrometeorological parameters and identifies sections of this guide where more detailed information can be found. Precipitation is a primary input into water budget calculations, and devices for measuring precipitation fall into two main categories: (1) *manual* gauges and (2) *recording* gauges. Measurement of *humidity* might be required during fieldwork for protection of health and safety and is required with most micrometeorological methods for measuring evapotranspiration. Other hydrometeorological measurements might be required for monitoring weather conditions, such as *temperature*, *wind speed*, and *wind direction*. Measurement or estimation of these same parameters, as well as *atmospheric pressure* and *insolation* or *solar radiation* measurement, might be required in order to quantify the evapotranspiration component of water budget studies (discussed below). Although numerous techniques and devices have been developed for hydrometeorological measurements, most of the parameters of interest usually can be estimated for purposes of vadose zone water budget studies by using data from nearby weather stations or interpolations using hydrometeorological tables or maps. Consequently, only those methods relevant to health and safety (temperature, humidity, wind speed, and direction) are likely to be used routinely during site investigations. Table A.5 identifies the specific hydrometeorological techniques or devices that are most commonly used for site investigations.

Evaporation and Evapotranspiration. Water that reaches the earth's surface can return to the atmosphere either by *evaporation* from free water surfaces or bare soil or by *transpiration* by plants. The term *evapotranspiration* (ET) specifically refers to the combined effects of evaporation and transpiration from the land surface, but also might be used loosely to refer to the combined effects of evaporation from water and soil surfaces and transpiration. ET is a critical component of vadose zone water budget calculations and is one of the most difficult of these components to measure accurately. The numerous methods that have been developed for measuring or estimating ET can be broadly classified as *water budget* or *balance* methods and *micrometeorological* methods. Table A.5 summarizes information on 10 water balance methods and 6 micrometeorological methods and identifies specific applications for each method (water evaporation, bare soil evaporation, evapotranspiration, and transpiration). Most of these methods are too complex and time-consuming for routine site investigations.

Lysimeters and *soil moisture monitoring* probably are the most commonly used methods for measuring evapotranspiration where site-specific data are required. Most vadose zone hydrologic models use *empirical equations* and data from nearby weather stations and published maps. The physically based *Penman equation* (and various methods developed as refinements and adaptations of the Penman equation) probably is the most commonly used method for estimation of evaporation or evapotranspiration, where some measurements of meteorological data are feasible, but the more complex measurements and instrumentation of other micrometeorological methods are not feasible.

7.1.4 Other Hydrologic Parameters

Miscellaneous Parameters. Other field-measurable hydrologic properties of the vadose zone, which might be of use in evaluating contaminant transport or design of remediation systems, include *sorptivity* (a measure of the capacity of a porous medium to absorb a wetting liquid), *soil diffusivity* (a single parameter of unsaturated soil that relates the hydraulic conductivity and water storage properties), and *available water capacity* (a measure of plant-available water in the soil). Sorptivity and diffusivity are properties that are significant in evaluating infiltration of water into the subsurface. Table A.3 indicates where more information can be obtained about these parameters.

Vadose Zone Water Flux.¹¹ Various methods are available to measure or estimate the amount of water that passes through the vadose zone and enters the ground-water system. A *water budget* uses a mass balance by measuring inflows, outflows, and storage changes in the area of interest. More often, a simplified water budget approach can be used, in which only changes in *soil moisture* or *matric potential* are measured. A variety of *tracers*, such as chloride and tritium, can be used to estimate the rate of recharge and water flux. Localized water flux can be measured using a *soil water flux meter*. Finally, a variety of *physical* and *empirical equations* can be used in combination with the methods above or using site-specific data on hydraulic conductivity or soil physical characteristics, such as texture and bulk density. *Tile drains* or *collection lysimeters* (Section 9.3.1 in Boulding, 1993/T7.5) also can be used to measure water flux in the vadose zone, provided the area of vertical infiltration is known and lateral ground-water flow can be excluded or quantified.

7.2 PREPARATION AND USE OF POTENTIOMETRIC MAPS

A water table or potentiometric map is one of the most basic and useful tools available for hydrogeologic characterization. A *water table* map usually refers to the hydraulic gradient of an unconfined aquifer (where the top of the saturated zone equals zero pressure head), and a *piezometric* (pressure) surface map usually refers to the pressure potentials of confined aquifers. Both types of maps are called *potentiometric* maps. In practice, the terms *water table*, *potentiometric*, and *piezometric* are often used interchangeably. A potentiometric map is developed by compiling ground- and surface-water level information from all available sources. [Section 7.2.1](#) addresses methods for measuring ground-water levels. [Section 7.2.2](#) describes how potentiometric contours are developed from water level information. Once a potentiometric map has been developed, interpretations of ground-water flow direction and quantity can be developed using flow nets ([Section 7.2.3](#)).

7.2.1 Water Level Measurement

Water level measurements in observation wells provide the basic data for a potentiometric map. Table A.6 summarizes information on nine techniques for measuring water levels in open or cased boreholes and three methods for measuring pressure head in flowing (artesian) wells. The *steel-tape* and *electric probe* methods are used most commonly for routine measurement of water levels. *Transducers* are used most commonly in aquifer tests where accurate measurement of changes in multiple wells is required in relatively short periods. The *air line method* is also useful in pumped wells where water turbulence may preclude using more precise methods. Pressure potential in the saturated zone also can be measured by burying *in situ* piezometers that sense pore pressure.

In addition to providing data for potentiometric maps, the water level in a monitoring well is measured and recorded prior to purging or sample collection. For detailed site investigations, each well requires an accurately surveyed reference point on the casing from which water level measurements are taken. For regional and local investigations (Section 5.1.2), estimating well elevations using a 7.5° topographic map is usually adequate. Documenting the static water levels for all wells at a site will provide historical information on the site's hydraulic conditions. This information may indicate changes in flow paths and documents seasonal changes in water levels. Without careful attention to these measurements, it may be impossible to interpret chemical concentration variability at the site.

¹¹ Appendix A does not identify these methods, but they are covered in Section 7.5 in Boulding (1993/T7.5). Individual subsections in that guide cover italicized terms in this section.

7.2.2 Plotting Equipotential Contours

The starting point for a potentiometric map is a base map. The base map identifies well locations and water level elevations in the well and other surface hydrologic features, such as streams, rivers, and water bodies. An accurate potentiometric map requires enough well observations to develop water table contours that do not miss important features of the flow system. Considerable interpretation and judgment may be required in developing contours when well data points do not seem to fit into a coherent pattern. For example, if water level data from wells are drawn from multiple sources, measurements in nearby wells may have been taken at different times of the year and may not be directly comparable. On the other hand, if all the data have been collected so as to minimize effects of short-term or seasonal fluctuations, examination of individual well characteristics may yield explanations for anomalous data points. For example, a single well data point that is far out of line with nearby wells may be tapping a different aquifer. If an anomalous well data point cannot be readily explained as being unrepresentative for any reason, then further field investigation may be required to determine whether any localized hydrogeologic conditions are causing the anomaly.

The contours on a potentiometric map are called *equipotential* lines, indicating that the water has the potential to rise to that elevation. In the case of a confined aquifer, however, it cannot reach that elevation unless the confining unit is perforated by a well. Potentiometric surface maps are essential to any ground-water investigation, because they indicate the direction in which ground water is moving and provide an estimate of the gradient, which controls ground-water velocity. As discussed in [Section 7.2.5](#), interpretations of flow directions in aquifers must take into account anisotropy and heterogeneity.

Potentiometric maps provide some information on aquifer homogeneity, provided that well data points are close enough to allow reasonably accurate contouring. A map of a uniform, homogeneous aquifer will have equally spaced equipotential lines and no dramatic changes in hydraulic gradient, because ground water is moving at about the same rate at all points in the aquifer. Irregularly spaced contours and differing hydraulic gradients in different areas of the aquifer indicate lateral changes in aquifer properties.

Preparing a potentiometric map involves plotting water level measurements on a base map and then drawing contours. In isotropic, porous media aquifers, the direction of ground-water flow is perpendicular to the ground-water contour lines. The next section on flow nets describes in more detail how contour maps can be used to infer the direction of ground-water flow. A minimum of three points is required to determine the general direction of ground-water flow. [Figure 7.3](#) shows a manual graphical depiction of ground-water contours, drawn based on water elevations in three wells. The difference in elevation between each well was calculated and divided into the distance between the wells. This distance was scaled on each line as tick marks that represent a change in elevation of one tenth of a foot. The lines connecting the points of equal elevation (27.0 and 27.5 ft in [Figure 7.3](#)) are potentiometric contours. Ground-water flow direction is on the path line perpendicular to the contours. The methods shown in [Figure 7.3](#) and [Figure 7.4](#), described below, are most appropriate for detailed site investigations where the scale is 1" = 200 ft or larger.

[Figure 7.4](#) illustrates a slightly different approach to determining the direction of ground-water flow from three well points. Steps in this solution involve:

1. Identifying the well that has the intermediate water level.
2. Calculating the position between the well having the highest head and the well having the lowest head at which the head is the same as that in the intermediate well.
3. Drawing a straight line between the intermediate well and the point identified in Step 2. This line represents a segment of the water level contour along which the total head is the same as that in the intermediate well.
4. Drawing a line perpendicular to the water level contour and through the well with the lowest (or highest) head. This indicates the direction of ground-water movement in an isotropic aquifer.

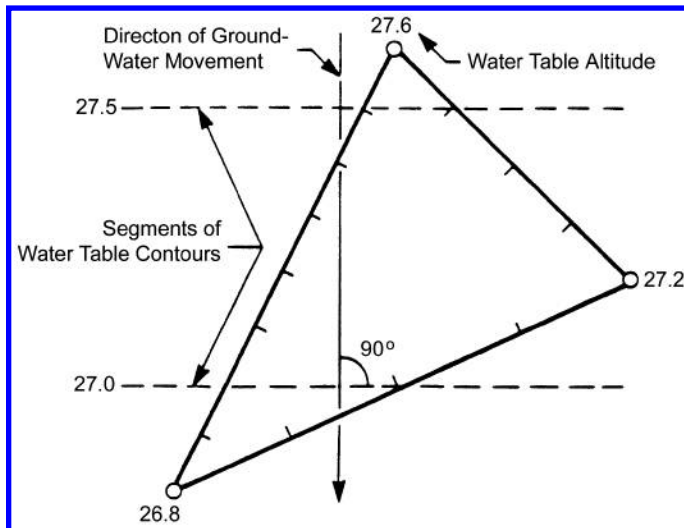


Figure 7.3 The generalized direction of ground-water movement can be determined by means of the water level in three wells of similar depth (U.S. EPA, 1987a, after Heath and Trainer, 1981).

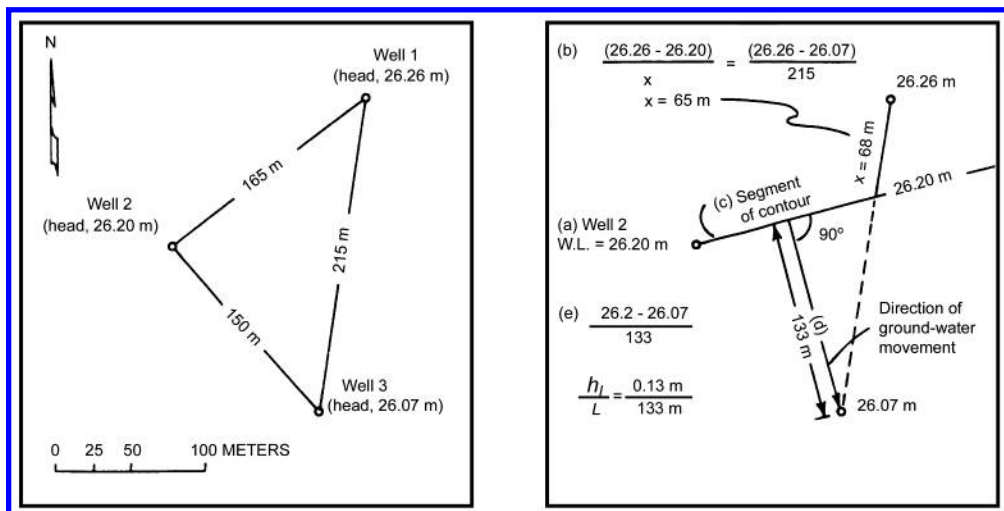


Figure 7.4 Alternative procedure for determination of equipotential contour and direction of ground-water flow in homogeneous, isotropic aquifer (Heath, 1983).

5. Dividing the difference between the head of the well and that of the contour by the distance between the well and the contour. This gives the hydraulic gradient.

A large number of well measurements is needed to develop an accurate potentiometric surface map. Geostatistical methods allow the estimation of water table elevations in unsampled locations where the water table is approximately parallel to the ground surface (Hoeksma et al., 1989).¹²

The most important consideration in preparing a potentiometric map is that the water level measurements should describe a single flow system in an aquifer. Section 7.2.4 describes in detail some common pitfalls in preparing potentiometric maps. Worksheet D-W1 provides a form for

¹² Hoeksma, R.J., R.B. Clapp, A.L. Thomas, A.E. Hunley, N.D. Farrow, and K.C. Dearstone. 1989. Cokriging Model for Estimation of Water Table Elevation. Water Resources Research 25(3):429–438.

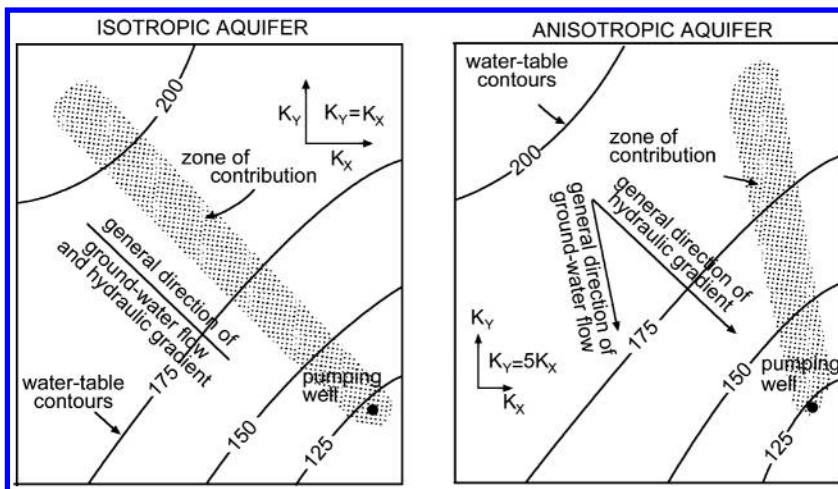


Figure 7.5 Effect of fracture anisotropy on the orientation of the zone of contribution to a pumping well (Bradbury et al., 1991).

compiling well information used to develop a potentiometric map. This information may prove helpful in evaluating individual well elevations that appear to be anomalous.

7.2.3 Flow Nets

A potentiometric surface map can be developed into a flow net by constructing flow lines that intersect the equipotential lines or contour lines at right angles. Flow lines are imaginary paths that trace the flow of water particles through the aquifer. Although there are an infinite number of both equipotential and flow lines, the former are constructed with uniform differences in elevation between them, while the latter are constructed so that they form, in combination with equipotential lines, a series of squares. A flow net carefully prepared in conjunction with Darcy's law allows estimation of the quantity of water flowing through an area and of the variability of transmissivity and hydraulic conductivity. Plan view flow nets are a valuable tool in delineating the zone of contribution to a well, as illustrated in Figure 10.3. Scott (1992)¹³ provides a good recent review of use of flow net analysis for aquifer identification. U.S. EPA (1986)¹⁴ provides guidance on use of flow net analysis for identifying areas of vulnerable hydrogeology under RCRA.

A standard flow net assumes that the aquifer is isotropic. Figure 7.5 illustrates how anisotropy in a fractured rock aquifer alters the direction of ground-water flow compared to that expected in an isotropic aquifer. When an aquifer is anisotropic, commonly the case in unconsolidated and sedimentary aquifers, the actual direction of ground-water flow will not be perpendicular to the equipotential contours. Instead, the direction of flow will deviate from the perpendicular at an angle that depends on the ratio of the horizontal to the vertical hydraulic conductivity.¹⁵

Several methods are available for determining the direction of flow lines where the degree of anisotropy is known. For potentiometric surface maps, Llakopoulos (1965)¹⁶ developed a graphical

¹³ Scott, D.M. 1992. An Evaluation of Flow Net Analysis for Aquifer Identification. *Ground Water* 30(5):755–764.

¹⁴ U.S. Environmental Protection Agency (EPA). 1986. Criteria for Identifying Areas of Vulnerable Hydrogeology Under RCRA: A RCRA Interpretive Guidance; Appendix B, Groundwater Flow, Net/Flow Line Construction and Analysis. EPA/530/SW-86-022B (NTIS PB 86-224979).

¹⁵ The discussion here assumes that the aquifer is anisotropic in only two directions, with the horizontal conductivity greater than the vertical conductivity, which is typical of horizontally layered sediments. Anisotropy in three directions is possible, but not amenable to simple graphical solutions for determining flow direction. Section 7.5.2 discusses methods for determining anisotropy in three dimensions.

¹⁶ Llakopoulos, A.C. 1965. Variation of the Permeability Tensor Ellipsoid in Homogenous Anisotropic Soils. *Water Resources Research* 1(1):135–142.

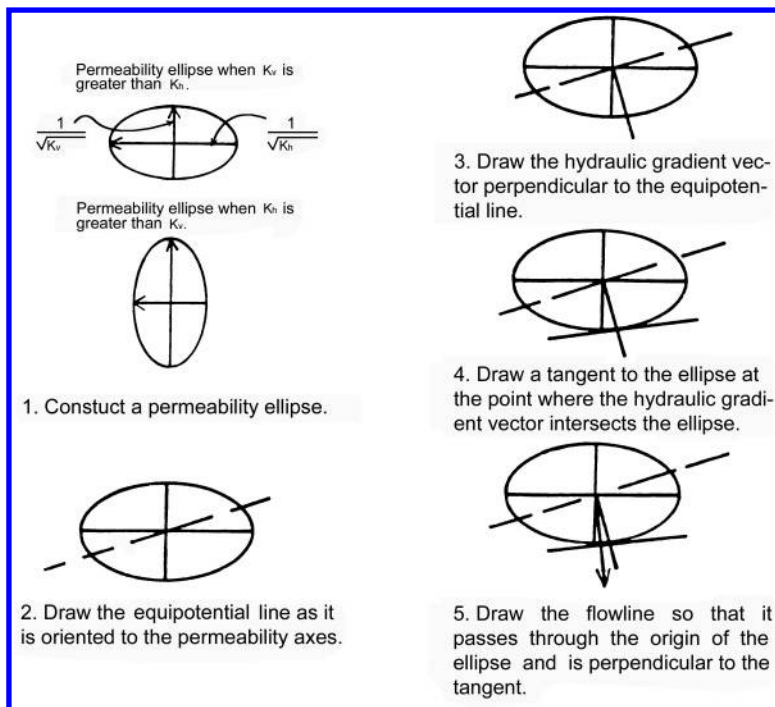


Figure 7.6 Steps in the determination of ground-water flow direction in an anisotropic aquifer (Fetter, 1981).

technique for determining this deviation. This technique uses a “permeability tensor ellipse,” which has semiaxes equal to the inverse square root of the principal permeability values. Figure 7.6 illustrates the five-step sequence for using this method. Fetter (1981)¹⁷ provides some additional guidance on using this technique. Section 7.5.2 provides some guidance on how to determine directional components of hydraulic conductivity in an aquifer.

When the ratio of a permeability ellipse is around 10:1 (not uncommon in sedimentary formations), the flow line diverges almost 45° from the expected direction when the axis of the equipotential line is at a 45° angle to the axis of maximum permeability. When interpreting flow direction from potentiometric maps, it is also important to know the angle of the axis of maximum permeability in relation to an equipotential line. For example, flow direction in an anisotropic aquifer *will* be perpendicular to an equipotential line if the axis of greater permeability in a permeability ellipse and the equipotential line are parallel. Fetter (1981 — footnote 17) provides an additional explanation of these relationships.

7.2.4 Common Errors in Contouring

Errors in contouring fall into two general categories: (1) failure to exclude data points that are not representative, and (2) failure to take into account subsurface features that change the distribution of potentiometric head as a result of aquifer heterogeneity or boundary conditions. The following are six situations in which contouring errors might occur:

1. *Failure to exclude well measurements from wells cased below the water table surface in recharge and discharge areas.* Figure 7.7a illustrates distortions in contouring that result from this effect, and Figure 7.7b shows the correct interpretation. The effect can perhaps be better understood by

¹⁷ Fetter, C.W., Jr. 1981. Determination of the Direction of Groundwater Flow. Ground Water Monitoring Review 1(3):28–31.

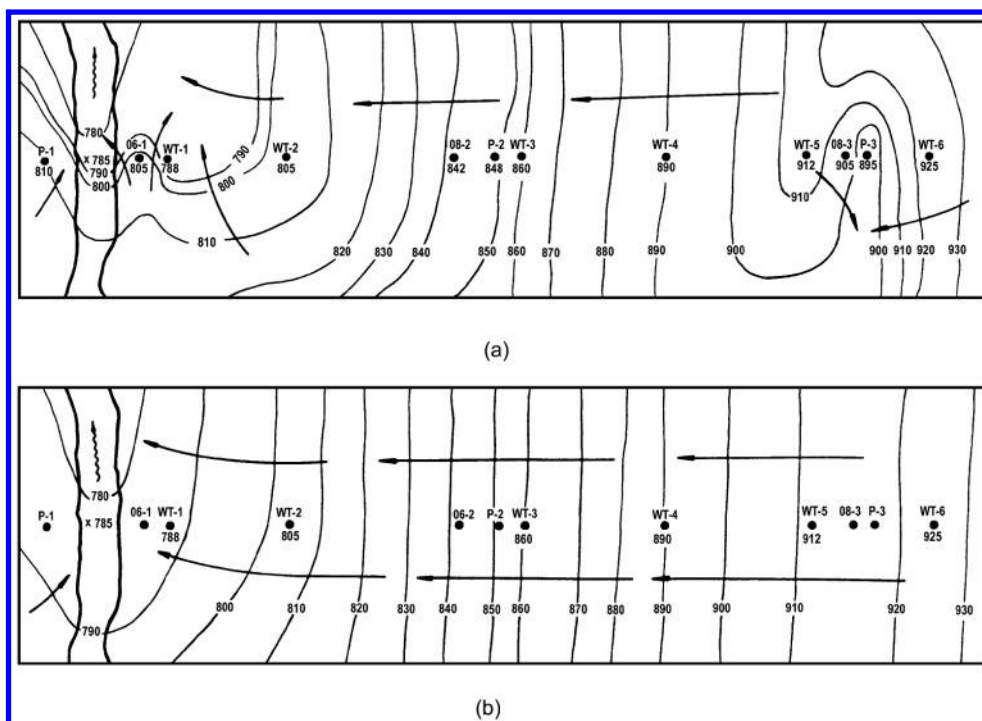


Figure 7.7 Effect of well level measurements in recharge and discharge areas: (a) incorrect contours; (b) correct contours after reinterpretation (Saines, 1981).

referring to the illustration of pressure-head distribution in recharge and discharge areas in Chapter 2 (Figure 2.10). In Figure 2.10 only well *c* gives an accurate reading of the water table surface.

2. *Failure to adjust contour lines in areas of topographic depressions occupied by lakes.* Figure 7.8a illustrates the incorrect and correct interpretations in this situation.
3. *Failure to recognize locally steep gradients caused by fault zones.* Figure 7.8b illustrates how conventional contouring methods erroneously portray the ground-water flow systems on the two sides of a fault.
4. *Use of measurements from wells tapping multiple aquifers.* Wells in which the screened interval includes multiple aquifers generally yield inaccurate water level or piezometric measurements because the measured head reflects the interaction between heads of the intersected aquifers. Figure 7.9 illustrates how the failure to differentiate measurements from wells completed in two aquifers, combined with a well that connects the two, results in an apparent depression in the potentiometric surface. An offsetting of nearby ground-water levels with similar elevations to form a Z shape is an indicator that a fault may be present.
5. *Failure to consider seasonal and other short-term fluctuations in well levels.* If an aquifer experiences seasonal high and low water tables, well measurements are not comparable unless they are taken at the same time of year. Other factors, such as dramatic changes in atmospheric pressure and precipitation events, might reduce the comparability of well measurements even if the measurements are taken at the same time of year.
6. *Failure to consider localized mounding or depression of the potentiometric surface from anthropogenic recharge or pumping.* Pumping wells create a cone of depression around the well (Section 2.6.6) with steepened hydraulic gradients. When the source of recharge is confined to a relatively small area, a localized mound develops with elevations increasing toward the center. Agricultural irrigation, artificial recharge using municipally treated wastewater, and artificial ponds and lagoons usually cause a mounding of water tables. Areawide recharge will reduce hydraulic gradients compared to natural aquifer conditions. These features are especially significant when they are located near a ground-water divide, because small shifts in the location of a divide may have a major impact on the direction in which contaminants flow.

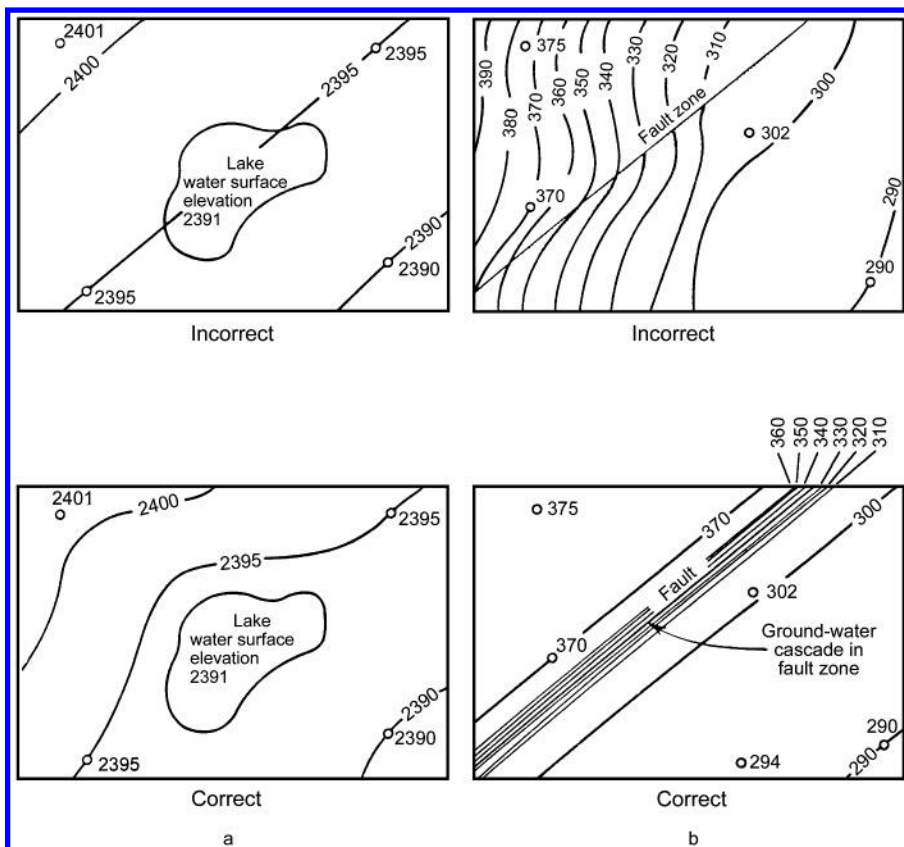


Figure 7.8 Common errors in contouring water table maps: (a) topographic depression occupied by lakes; (b) fault zones (Davis and DeWiest, 1966).

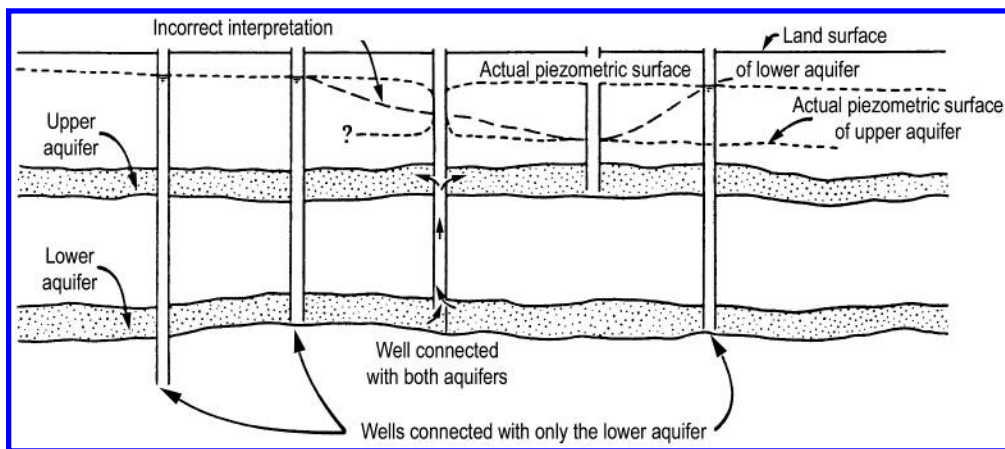


Figure 7.9 Error in mapping potentiometric surface due to mixing of two confined aquifers with different pressures (Davis and DeWiest, 1966).

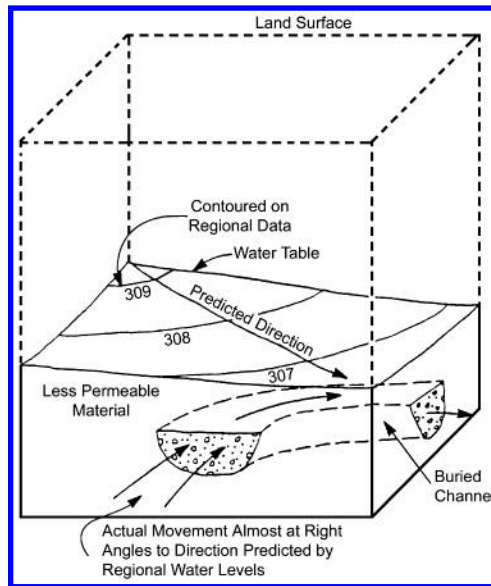


Figure 7.10 Divergence from predicted direction of ground water resulting from aquifer heterogeneity (Davis et al., 1985).

7.2.5 Common Errors in Interpretation

As noted earlier, ground-water flow is perpendicular to contours on a potentiometric map if the aquifer is isotropic. However, failure to account for anisotropy and heterogeneities in an aquifer can result in significant errors in the interpretation of ground-water flow direction. Following are three situations in which flow direction will differ from that indicated by conventional flow net construction using an *accurate* potentiometric map:

1. *Homogeneous, anisotropic aquifers.* Figure 7.5 illustrates how flow direction can diverge from flow in an isotropic aquifer. Section 7.2.3 discussed how to determine the direction of flow in this situation.
2. *Heterogenous aquifers with contrasting hydraulic conductivity.* Figure 7.10 illustrates an example of divergence of flow from the direction predicted by ground-water contours as a result of a buried channel of higher permeability oriented across the direction of the potentiometric surface. This kind of divergence is difficult to predict accurately. Careful examination of well logs for the areal distribution of materials with contrasting hydraulic conductivity and the use of tracer tests may help modify flow direction interpretations when this situation occurs.
3. *Backwater effects in discharge areas.* Short-term reverses in the direction of ground water occur when streams or rivers are at high stage (Figure 2.6). These effects can extend for hundreds of feet from the stream edge. Wells that may be subject to bank storage can be identified by monitoring changes in water levels in response to stream flood events.

Reverse Flow of Contaminants. Several situations can cause contaminants to flow in a different direction from that indicated by flow net construction using a potentiometric map. Dissolved contaminants follow the direction of ground-water flow. Attention should be paid, however, to the possibility of localized flow patterns that run against the general direction of ground-water flow (mounding of ground water caused by ponds and lagoons and backwater effects in discharge areas). Dense leachates and nonaqueous phase liquids (NAPLs), on the other hand, can flow in an entirely different direction from that of ground-water flow if the slope of the geologic material forming the

base of the aquifer does not follow the potentiometric surface. Figure 4.10 illustrates a dense NAPL flowing in the opposite direction of ground-water flow as a result of geologic controls.

7.3 FIELD AND LABORATORY MEASUREMENT OF AQUIFER PARAMETERS

Potentiometric maps provide a useful starting point for developing an understanding of the hydrogeology of a site or area. Site-specific investigations usually require more extensive characterization in the form of field and laboratory tests and measurements of aquifer parameters. These methods can be broadly classified as (1) shallow water table tests (Section 7.3.1), (2) well tests (Section 7.3.2), (3) other field tests (Section 7.3.3), and (4) laboratory measurements (Section 7.3.4).

7.3.1 Shallow Water Table Tests

Table A.7 provides summary information on 10 relatively simple techniques that are available for measuring hydraulic conductivity where there is a shallow water table (generally less than 1 m). The *auger hole method* is the most widely used. This method involves boring an open hole below the water table, removing water, and measuring the water level at intervals until water reaches the original level. Other methods may be more appropriate for different site conditions. This type of test measures only hydraulic conductivity of the upper part of the aquifer and is most useful where potential contamination from agricultural chemicals is a concern. Because the tests are relatively fast and inexpensive, they may be useful for measuring spatial variability hydraulic conductivity.

7.3.2 Well Tests

Well tests are the most common and versatile methods for directly measuring aquifer parameters. They fall into three main categories: (1) single-well slug tests, (2) pumping tests (single and multiwell), and (3) packer tests (single- and two-packer). *Slug* tests involve measuring the rate at which water in a well returns to its initial level after (1) a sudden injection or withdrawal of a known volume of water from a well, or (2) instantaneous displacement by a float, weight, or change in pressure. *Aquifer pump* tests involve removing water from a well over a period from days to possibly weeks and measuring the changes in water levels in the pumping well (single-well test) and adjacent observation wells (multiple-well test). *Packer* tests are used to measure hydraulic conductivity in isolated sections of a borehole by monitoring the time-pressure response of the aquifer section when water is injected. The data from well tests are plotted and matched against curves calculated using analytical solutions to ground-water flow appropriate for the well construction and aquifer characteristics.

As Table A.7 indicates, all well tests measure hydraulic conductivity, but the types of other aquifer parameters that can be obtained from these tests vary. Slug and packer tests measure hydraulic conductivity of relatively small portions of an aquifer adjacent to the borehole, but are relatively easy to conduct and consequently are well suited for characterizing aquifer heterogeneity. Aquifer pump tests are more complex and difficult to carry out, but provide information on a larger portion of the aquifer. Pumping tests are the only well test method that information on the aquifer storage properties of an entire aquifer. Most slug tests provide relatively little information on aquifer storage properties.

A key element of aquifer testing is the selection of an appropriate analytical solution, or type curve developed from an analytical solution, to analyze the test data. Characteristics of the aquifer should not violate the assumptions used in developing the analytical solution. Worksheet D-W4 should be used to identify key aquifer characteristics that affect aquifer test results. ASTM D4043 (Table A.14) provides guidance on the selection of aquifer well test methods. Figure 7.11 provides a decision tree for the selection of methods covered in that guide. Table 7.6 provides an index of

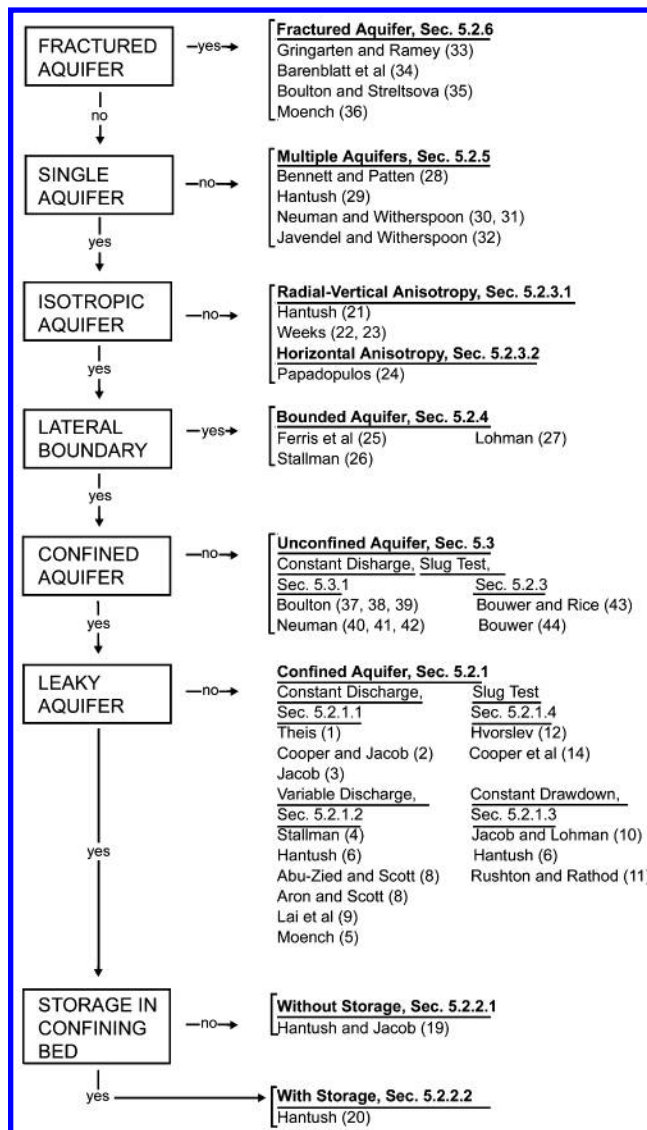


Figure 7.11 Decision tree for selection of aquifer test methods (ASTM D4043-91).

references that give analytical solutions to aquifer test data according to pump test conditions and type of test. This table includes quite a few references not cited in ASTM D4043 and is most likely to be useful when aquifer conditions depart significantly from assumptions in the most commonly used analytical methods.

Well test methods are best suited for porous media, and most methods tend to give misleading results where fracture or conduit flow is an important component of ground-water flow. [Section 7.5.4](#) discusses how the response of an aquifer to pumping can be used to evaluate whether fracture flow is a significant component of flow in an aquifer.

Single-Well Tests. Hydraulic conductivity values can be estimated by slug or bail tests using a single well or piezometer. These tests record the response of the well or piezometer to a sudden change in the water level and provide *in situ* values representative of a small volume of the porous material in the immediate vicinity of the piezometer. The water level can be changed by introducing a known quantity of water, slugging the well, or removing a known quantity of water with a bailer.

These methods are suitable where changes in water level take place slowly (minutes to hours) and accurate measurements can be made. Table 7.5 identifies major references describing various methods, including (1) shallow water table tests, (2) slug tests, and (3) packer tests. Another type of single-well test is the *step drawdown* test, where the well is pumped at successively greater discharge rates for relatively short periods of time and the drawdown at each rate is recorded. The step drawdown test was developed for use in wells that may have turbulent flow (Jacob, 1946b; Bierschenk, 1964/T7.6). Butler et al. (2002)¹⁸ described procedures for performing slug tests at more than one level in a single direct-push hole.

Multiple-Well Aquifer Tests. Multiple-well aquifer tests provide *in situ* measurements that are averaged over a large aquifer volume. Aquifer test data yield information on both the storativity and transmissivity of the aquifer. The design of a basic aquifer pump test consists of a pumping well that is pumped at a constant rate and at least one observation well. The wells are located far enough from any boundaries so that drawdown trends are not masked by the boundary effects. The interpretation of pump test results requires a good understanding of the hydraulics of ground-water flow. Drawdown data are collected from both the pumping well and the observation well(s); however, measurements in the pumping well may be less reliable due to turbulence caused by pumping. The diameter of an observation well should be just large enough to allow for the accurate measurement of the water levels.

The two most common methods for calculating the aquifer coefficients from the drawdown data are (1) the Theis method (Theis, 1935/T7.6), which involves using the Theis nonequilibrium well equation and curve matching on a log-log plot, and (2) the Jacob method (Cooper and Jacob, 1946/T7.6), which uses a simplified version of the Theis equation and involves plotting the data on a semi-log plot. The Jacob's equation yields an approximation of the Theis analytical solution that slightly reduces the accuracy of predicted head changes at locations far from the well unless pumping is long enough to approach equilibrium or steady-state conditions.

The principal assumptions in the Theis equation are:

- The aquifer is homogenous and isotropic.
- The aquifer is of infinite areal extent, relative to the effects of the well (no boundaries).
- The well is screened over the entire saturated thickness of the aquifer.
- The saturated thickness of the aquifer does not vary as a result of the operation of the well.
- The well has an infinitesimal diameter so that waters in storage in the casing represent an insignificant volume.
- Water is removed from or injected into the aquifer with an instantaneous change in the piezometric head.

Although most aquifers do not conform to all the theoretical conditions assumed by Theis and Jacob, these equations and their graphic relationships are often quite satisfactory as a general indicator of conditions. Numerous analytical equations have been developed for situations where the assumptions in the Theis equation do not apply. These conditions include (1) partially penetrating wells, (2) anisotropic aquifer conditions, and (3) leaky aquifers (confined aquifers where there is significant movement of water upward or downward through the overlying confining layer). Table 7.6 indexes references containing analytical solutions under various combinations of these conditions.

Conventional multiple-well aquifer tests provide average hydraulic properties over a large area. A new multiple-well aquifer test method, called *hydraulic tomography*, has been developed that allows characterization of the vertical and lateral spatial distribution of hydraulic conductivity in a heterogeneous aquifer.¹⁹ Packers are used to separate fully screened wells into many vertical

¹⁸ Butler, Jr., J.J., J.M. Healey, L. Zheng, W. McCall, E.J. Garnett, and S.P. Loheide, II. 2002. Hydraulic Tests with Direct-Push Equipment. *Ground Water* 40:25–36.

¹⁹ Butler, J.J., Jr., C.D. McElwee, and G.C. Bohling. 1999. Pumping Tests in Networks of Multilevel Sampling Wells: Motivation and Methodology. *Water Resources Research* 35:3553–3560. Yeh, T.C.J. and S. Liu. 2000. Hydraulic Tomography: Development of a New Aquifer Test Method. *Water Resources Research* 36:2095–2195.

intervals. Water is pumped from or injected into one of the intervals until steady flow conditions are achieved. Hydraulic head responses of the aquifer at other intervals are measured to obtain a set of head/discharge (or recharge) data. Sequentially pumping or injecting water at different intervals in different wells provides many head/discharge or head/recharge data sets that can be analyzed using geostatistical methods.

7.3.3 Other Field Tests

Tracer Tests. Table A.7 summarizes the types of hydrogeologic information that can be obtained using ground-water tracers. Chapter 8 discusses use of tracers in some detail.

Other Techniques. Table A.7 also identifies 10 miscellaneous techniques for aquifer characterization. Potentiometric maps have been discussed in some detail in [Section 7.2](#). Numerous procedures have been developed for hydrologic analysis based on the *water balance* or *budget* for an area. A simple water balance equation is as follows (Dunne and Leopold, 1978/T2.4):

$$\Delta GWS = P - I - AET - OF - \Delta SM - GWR \quad (7.1)$$

where:

ΔGWS = change in ground-water storage

P = precipitation

I = interception

AET = actual evapotranspiration

OF = overland flow

ΔSM = change in soil moisture

GWR = ground-water outflow

Many variants are possible. The usual procedure is to formulate the equation with the parameter of interest on the left-hand side and the other components that define the hydrologic system of an area or aquifer of interest on the right-hand side. [Table 7.5](#) identifies references that are good sources for further information on the water balance approach. In an unconfined aquifer, changes in soil moisture profiles in response to changes in the water table provide an alternative to pumping tests for measurement of *specific yield* (see [Section 4.5.2](#) in Boulding, 1993/T7.5).

The barometric efficiency ([Section 2.5.5](#)) of confined aquifers, a measure of the response of a confined aquifer to changes in atmospheric pressure, is being increasingly used to estimate aquifer storage properties and transmissivity (see, for example, Ritzi et al., 1991).²⁰ Table A.7 also identifies some of the more commonly used borehole geophysical logging methods for measuring aquifer parameters. These methods are used primarily for characterizing aquifer heterogeneity vertically within a single borehole and laterally between boreholes.

7.3.4 Laboratory Measurements

Laboratory methods for measuring hydraulic conductivity provide an important complement to field tests (Petsonk, 1988).²¹ Laboratory measurements of the properties of aquifer materials require the collection of undisturbed soil cores using thin-wall samplers for unconsolidated materials or rotating core samplers for rock ([Section 9.4.1](#)). Two commonly used methods for laboratory measurement of hydraulic conductivity are the *constant-head* and *falling-head permeameters* (ASTM D2434 and D5084/TA.14; Klute and Dirksen, 1986 — footnote 8). In a constant-head

²⁰ Ritzi, R.W., S. Sorooshian, and P.A. Hsieh. 1991. The Estimation of Fluid Flow Properties from the Response of Water Levels in Wells to the Combined Atmospheric and Earth Tide Forces. *Water Resources Research* 27(5):883–893.

²¹ Petsonk, A.M. 1988. Hydraulic Conductivity Measurements in Unsaturated Media: Materials vs. Lab Methods. *Ground Water Monitoring Review* 8(2):50–51.

permeameter, the hydraulic gradient is kept constant, while the discharge is recorded. In a falling-head permeameter, the hydraulic gradient and the discharge decrease with time. The constant-head system is best suited to samples with hydraulic conductivities greater than 0.01 cm/min, while the falling-head system is suited to samples with lower hydraulic conductivity (Klute and Dirksen, 1986 — footnote 13). Each sample is tested several times under different hydraulic gradients, and an average hydraulic conductivity is calculated. Hydraulic conductivity can also be measured using centrifugation (Alemi et al., 1976).²² Effective porosity is another parameter that is measured in the laboratory (ASTM D4404/TA.14; Horton et al., 1988).²³ Total porosity is usually calculated by measuring the dry bulk density of a known volume of soil or rock and assuming an average particle density.

A disadvantage of measuring aquifer properties from core samples is that they sample a very small portion of the aquifer. Consequently, values for hydraulic conductivity tend to be low compared to values measured in the field, which include the effects of secondary porosity and aquifer heterogeneities (Bradbury and Muldoon, 1990; Bryant and Bodocsi, 1987).²⁴ [Figure 7.17](#) and [Figure 7.18](#) ([Section 7.5.4](#)) illustrate the effect of differences in scale of measurement on observed hydraulic conductivity in karst aquifers. On the other hand, laboratory measurement of multiple samples can provide valuable information on the vertical and lateral variabilities of aquifer properties. This information is especially important for constructing grids for three-dimensional aquifer modeling ([Section 10.2.4](#)).

7.4 ESTIMATION OF SUBSURFACE HYDROLOGIC PARAMETERS

The critical aquifer parameters of porosity, specific yield, and hydraulic conductivity are typically not measured for most water wells. Therefore, the initial stages of hydrogeologic investigations often require estimation for one or more of these parameters. Estimation requires some knowledge of the geologic character of the aquifer and data on the ranges or typical values that have been measured in similar settings elsewhere. When used cautiously, such estimates can increase the effectiveness and reduce the cost of any required field measurements and additional data collection.

7.4.1 Estimation from Soil Survey Data

When aquifers are in unconsolidated deposits and the water table is relatively near the surface, soil surveys published by the Soil Conservation Service (SCS) of the U.S. Department of Agriculture are an excellent source of information about the character of subsurface materials and soil hydrologic properties. A two-page soil series description sheet and a two-page soil survey interpretation sheet are available for every established soil series in the U.S. [Table 7.1](#) summarizes the information that is available from these records. The table highlights in boldface type the information that may be useful for geologic and hydrogeologic interpretations.

SCS soils surveys typically do not provide any detailed information deeper than 5 ft below the ground surface, but they do provide a general indication of the type of deeper geologic materials. In the absence of, or in combination with, other geologic data about the area of interest, this

²² Alemi, M.H., D.R. Nielsen, and J.S. Biggar. 1976. Determining the Hydraulic Conductivity of Soil Cores by Centrifugation. *Soil Science Society of America Journal* 40:212–218.

²³ Horton, R., M.L. Thompson, and J.F. McBride. 1988. Determination of Effective Porosity of Soil Materials. EPA/600/2-88/045 (NTIS PB88-242391).

²⁴ Bradbury, K.R. and M.A. Muldoon. 1990. Hydraulic Conductivity Determinations in Unlithified Glacial and Fluvial Materials. In: *Ground Water and Vadose Zone Monitoring*, D.M. Nielsen and A.I. Johnson (eds.), ASTM STP 1053, American Society for Testing and Materials, Philadelphia, pp. 138–151. Bryant, J. and A. Bodocsi. 1987. Precision and Reliability of Laboratory Permeability Measurements. EPA/600/2-86/097 (NTIS PB87-113791).

Table 7.1 Types of Data Available on SCS Soil Series Description and Interpretation Sheets^a

Soil Series Description Sheet	
Taxonomic class	
Typical soil profile description	
Range of characteristics	
Competing series	
Geographic setting	
Geographically associated soils	
Drainage and permeability	
Use and vegetation	
Distribution and extent	
Location and year series was established	
Remarks	
Availability of additional data	
Soil Survey Interpretations Sheet	
Estimated soil properties (major horizons)	
Texture class (USDA, Unified, and AASHTO)	
Particle size distribution	
Liquid limit	
Plasticity index	
Moist bulk density (g/cm³)	
Permeability (in./h)	
Available water capacity (in./in.)	
Soil reaction (pH)	
Salinity (mmhos/cm)	
Shrink–swell potential	
Sodium absorption ratio	
Cation exchange capacity	
Calcium carbonate (%)	
Gypsum (%)	
Organic matter (%)	
Corrosivity (steel and concrete)	
Erosion factors (K, T)	
Wind erodability group	
Flooding (frequency, duration, months)	
High water table (depth, kind, months)	
Cemented pan (depth, hardness)	
Bedrock (depth, hardness)	
Subsidence (initial, total)	
Hydrologic group	
Potential frost action	
<i>Note:</i> Boldface = information that may be useful for geologic and hydrogeologic interpretations.	
^a Most of this information is included in published SCS county soil surveys, if available.	
<i>Source:</i> Boulding (1993c).	

information provides a basis for estimating porosity, specific yield, and hydraulic conductivity, as discussed in the next section.

If a published SCS soil survey is available for a site of interest, the information in Table 7.1 will be contained in the report, but scattered in different locations. It is probably useful to obtain the single soil series descriptions and interpretations (usually available from the SCS state office as a four-page handout) as a convenient consolidated reference for the soil series of interest. However, this sheet should be checked against data in the published soil survey, since the soil survey often will have additional data specific to the county in question.

7.4.2 Estimation from Aquifer Matrix Type

Porosity, specific yield, and hydraulic conductivity fall within reasonably well-defined ranges for most aquifer materials, although some rocks, such as basalt, encompass the entire natural range of hydraulic conductivity (see Figure C.3). The following tables and figures in Appendix C provide information compiled from a variety of sources:

Porosity: Table C.1 and Figures C.1 and C.3

Specific Yield: Table C.2 and Figures C.1, C.2, and C.15

Hydraulic Conductivity: Table C.3 and Figures C.3 through C.15

Sources may differ somewhat in the ranges given for a specific aquifer material. These differences probably exist because of slight differences in the way the material has been defined or because different sets of data measurements were examined. Below are some guidelines for estimating porosity, specific yield, and hydraulic conductivity for a specific aquifer:

1. Define the nature of the aquifer material as thoroughly as possible, using available well logs, soil surveys, geologic maps, and hydrogeologic maps.
2. On the well data worksheet, enter values (or ranges) for porosity, specific yield, and hydraulic conductivity from all sources in the tables and figures identified above that provide data on similar or related aquifer materials.
3. If the sources provide different ranges for the same material, review the tables and figures again to see if any subtle distinctions in the way the materials are described might make one more appropriate for the aquifer in question.
4. Select a range of values that seem reasonable based on the information available, and enter the range in the well/aquifer data Worksheet D-W1. For aquifer materials with a wide possible range, the range should be narrowed based on the presence or absence of characteristics that tend to increase or decrease the parameter in question (Table 7.2).

Table 7.2 identifies factors that tend to increase or decrease porosity, specific yield, and hydraulic conductivity. Interactions between factors may mitigate or offset a given tendency. Many of the same factors tend to increase and decrease all three factors, but there are some interesting differences. Porosity tends to decrease as particle size increases, whereas the reverse is true for hydraulic conductivity. This is because clays have a high porosity, but the size of pores is so small that water moves very slowly. Specific yield, on the other hand, is typically highest in sandy materials and generally decreases with larger and smaller particle sizes. This is because as particle size increases

Table 7.2 Aquifer Characteristics Affecting Porosity, Specific Yield, and Hydraulic Conductivity

Parameter	Tendency to Increase	Tendency to Decrease
Porosity	Well sorted (same size)	Poorly sorted
	Rounded particles	Irregular-shaped particles
	Stratified	Unstratified
	Small particle size	Large particle size
	Unconsolidated	Cemented/lithified
Specific yield	High secondary porosity	Low secondary porosity
	Sand particle size	Gravel, silt, clay
	High secondary porosity	Low secondary porosity
Hydraulic conductivity	Gravel, sand	Clay
	Well sorted (same size)	Poorly sorted
	Stratified	Unstratified
	Unconsolidated	Cemented/lithified
	High secondary porosity	Low secondary porosity

Source: Boulding (1993c).

to gravel, the pore space available to store water decreases, and as particle size decreases, water drains less readily from the smaller pores.

7.4.3 A Simple Well Test for Estimating Hydraulic Conductivity

The next section describes more complex well tests for measuring aquifer parameters, but a rough estimate of hydraulic conductivity is possible if three easily measured parameters are known: (1) the *static* water level prior to any pumping, (2) the normal well pumping rate, and (3) the level to which water drops after pumping starts and stays when inflow into the well equals the pumping rate. *Drawdown* is the difference between the static level and the level to which the water drops during pumping. The discharge rate of the well divided by the drawdown is the *specific capacity*, not to be confused with *specific yield* (Section 2.6.1). The specific capacity indicates how much water the well will produce per foot of drawdown. It can be calculated by the following equation:

$$S_c = Q/wd \quad (7.2)$$

where:

S_c = specific capacity

Q = discharge rate, gallons per minute (gpm)

wd = well drawdown, feet (elevation of static water surface – elevation when pumped)

If a well produces 100 gpm and the drawdown is 8 ft, the well will produce 12.5 gpm for each foot of available drawdown. Multiplying specific capacity by 2000 gives a crude estimate of transmissivity ($T = 2000 \times \text{specific capacity}$ in units of gpd/ft), which in turn can be used to estimate hydraulic conductivity by rearranging Equation 7.2:

$$K = T/b = 2000 \times S_c/b \quad (7.3)$$

However, transmissivity estimates based on specific capacity measurements are commonly low because of well construction details (e.g., screen length is less than the thickness of the aquifer). Worksheet D-W1 contains space for recording information for calculating the specific capacity of a well.

7.5 SPECIAL CONSIDERATIONS IN HYDROGEOLOGIC MAPPING

The methods described so far all contribute in some fashion to the process of hydrogeologic mapping. Certain field conditions require special approaches to field investigations when they are present. These include (1) identification of aquifer boundaries (Section 7.5.1); (2) characterization of aquifer heterogeneity or anisotropy (Section 7.5.2); (3) assessing the presence and degree of confinement in aquifers (Section 7.5.3); and (4) characterization of fractured rock and karst aquifers.

7.5.1 Delineation of Aquifer Boundaries

Identification of subsurface aquifer boundaries is an essential part of selecting analytical solutions for aquifer tests and computer modeling of ground-water systems characterized by porous media flow (see Section 7.5.4 for approaches to delineating aquifer boundaries in fractured rock and karst aquifers). They must also be known when delineating a well's zone of contribution (ZOC) for wellhead protection areas (Section 11.2.1). Ground-water divides upgradient from a well can be readily identified using a potentiometric surface map (Section 7.2).

Section 2.5.6 discusses other major types of aquifer boundaries. Worksheet D-W3 can be used to identify possible aquifer boundaries that may affect a well. Figure 2.13 provides illustrations of most of these types of boundaries. Determining the distance from the boundary to the well will help identify those boundaries that might be most significant for purposes of wellhead protection area delineation.

Additional analysis using simple analytical methods for calculating drawdown (Table 7.6) may be required to determine whether an aquifer boundary actually functions as a boundary to the well's ZOC. For example, a stream downgradient from a well would represent a potential boundary, but would only serve as an actual boundary if the well's zone of influence (ZOI) (see definitions in Table 11.2) extends to the stream.²⁵ Similarly, an impermeable boundary that lies outside the upgradient ZOC would not represent an aquifer boundary to the ZOC.

7.5.2 Characterization of Aquifer Heterogeneity and Anisotropy

Failure to characterize aquifer heterogeneity and anisotropy can have a number of undesired consequences for contaminant investigations (Section 7.2.5). They are also important considerations in delineation of wellhead protection areas (Section 11.2). Using an average value for hydraulic conductivity in any of the simple wellhead protection area (WHPA) delineation methods summarized in Table 11.1 will underestimate the time of travel or zone of influence based on drawdown, because contaminants will travel faster in fractures or layers of higher permeability, if they are present. Aquifer anisotropy or heterogeneity can result in incorrect delineation of WHPA boundaries based on potentiometric maps and flow net analysis. Figure 7.5 illustrates this effect in an anisotropic aquifer, and Figure 7.10 shows how this can happen in a heterogeneous aquifer. Consequently, any hydrogeologic investigation should assess the presence and degree of variability of hydrologic properties vertically and laterally.

Any method that allows measurement or qualitative observation of the similarities and differences in a particular aquifer characteristic in a vertical or horizontal direction allows assessment of whether an aquifer is homogeneous or heterogeneous. Table 7.3 summarizes a number of field methods that are commonly used or especially well suited for this purpose. Drill logs and geophysical borehole logs allow assessment of vertical changes in lithology, porosity, and permeability. Packer tests allow measurement of variations in hydraulic conductivity at different intervals. Surface geophysical methods, such as seismic refraction, seismic reflection, and electrical resistivity soundings, also allow less precise mapping of vertical changes in lithology.

An accurate potentiometric surface map (Section 7.2.2) is one of the most valuable ways to evaluate aquifer heterogeneity. Hydrochemical maps also provide information that can be specifically related to the hydrogeology of an area. Tracer tests (Chapter 8) may indicate whether fracture flow or zones of high permeability exist. This is indicated when the time of travel of the tracer is faster than the time of travel calculated from estimated aquifer properties or values measured by well tests. Geologic cross sections, isopach maps, and structural maps, which are generally based on interpolations between borehole logs, allow assessment of lithologic variations. Surface geophysical methods allow relatively rapid measurement of lateral variations in lithology, structure, and water quality where no better subsurface information is available. However, some verification with subsurface borehole data is required.

Geostatistical methods, originally developed for characterizing mineral ore bodies (Section 5.6.2), have been found to be increasingly useful tools for characterizing the variability of aquifer parameters. For example, Poeter and Belcher (1991)²⁶ recently described a method for characterizing porous medium heterogeneity by "inverse plume analysis," in which the spatial distribution of

²⁵ If the ZOI is within several hundred feet of the stream, some consideration should be given to the possibility of bank storage effects during flooding (Figure 2.6).

²⁶ Poeter, E.P. and W.R. Belcher. 1991. Assessment of Porous Media Heterogeneity by Inverse Plume Analysis. *Ground Water* 29(1):56–62.

Table 7.3 Summary of Methods for Characterizing Aquifer Heterogeneity

Method	Properties	Comments
Vertical Variations		
Drill logs	<ul style="list-style-type: none"> • Changes in lithology • Aquifer thickness • Confining bed thickness • Layering of high/low hydraulic conductivity • Variations in primary porosity (based on material description) 	Basic source for geologic cross sections; descriptions prepared by geologist preferred over those by well drillers; continuous core samples provide more accurate descriptions
Electric logs	<ul style="list-style-type: none"> • Changes in lithology • Changes in water quality • Strike and dip (dipmeter) 	Require uncased hole and fluid-filled borehole
Nuclear logs	<ul style="list-style-type: none"> • Changes in lithology • Changes in porosity (gamma-gamma) 	Suitable for all borehole conditions (cased, uncased, dry, and fluid-filled)
Acoustic and seismic logs	<ul style="list-style-type: none"> • Changes in lithology • Changes in porosity • Fracture characterization • Strike and dip (acoustic televiewer) 	Requires uncased or steel cased hole, and fluid-filled hole
Other logs	<ul style="list-style-type: none"> • Secondary porosity (caliper, television/photography) • Variations in permeability (fluid-temperature, flowmeters, single borehole tracing) 	Require open, fluid-filled borehole; relatively inexpensive and easy to use
Packer tests	<ul style="list-style-type: none"> • Hydraulic conductivity 	Single-packer tests used during drilling; double-packer tests after hole completed
Surface geophysics	<ul style="list-style-type: none"> • Changes in lithology (resistivity, electromagnetic induction, time domain EM, seismic refraction) 	Requires use of vertical sounding methods for electrical and electromagnetic methods
Lateral Variations		
Potentiometric maps	<ul style="list-style-type: none"> • Changes in hydraulic conductivity 	Based on interpretation of the shape and spacing of equipotential contours
Hydrochemical maps	<ul style="list-style-type: none"> • Changes in water chemistry 	Requires careful sampling, preservation, and analysis to make sure samples are representative
Tracer tests	<ul style="list-style-type: none"> • Time of travel between points • Potential distribution of contaminants 	Requires injection point and sufficient downgradient collection points; essential for investigation of flow in karst
Geologic maps and cross sections	<ul style="list-style-type: none"> • Changes in formation thickness • Structural features, faults 	Result from correlation features observed at the surface and in boreholes
Isopach maps	<ul style="list-style-type: none"> • Variations in aquifer and confining layer thickness 	Distinctive strata with large areal extent required
Geologic structure maps	<ul style="list-style-type: none"> • Stratigraphic and structural boundary conditions affecting aquifers 	See Table 7.4
Surface geophysics	<ul style="list-style-type: none"> • Changes in lithology (seismic) • Structural features (seismic, GPR, gravity) • Changes in water quality/contaminant plume detection (ER, EMI, GPR) 	Interpretations require verification using subsurface borehole data

Source: Boulding (1993c).

contaminant concentrations is used to evaluate variation in aquifer properties. Both of these approaches, however, require a relatively high density of subsurface observations. See also the description of hydraulic tomography described in [Section 7.3.2](#). Special approaches to aquifer characterization are typically required in fractured rock and karst limestone aquifers, as discussed in [Section 7.5.4](#).

Measurement of Anisotropy. Measurement of anisotropy requires determination of the direction of maximum and minimum hydraulic conductivity. In a homogenous, horizontally layered aquifer, the direction of minimum conductivity is usually assumed to be in the vertical direction,

and the maximum in the horizontal direction (Section 2.5.3). Fetter (1981 — footnote 17) suggests collecting undisturbed cores for measurement of vertical hydraulic conductivity in the laboratory (Section 7.3.4) and using slug tests (Section 7.3.2), which primarily measure horizontal conductivity, in the test hole. This procedure also requires installation of at least three wells to accurately determine the orientation of equipotential lines.

A number of other methods have been developed for estimating anisotropy in layered aquifers using pumping tests. Most require a minimum of two or three observation wells, in addition to a pumping well, to measure the degree of departure from a circular cone of depression that occurs in an isotropic aquifer. In fractured rock aquifers, anisotropy can occur in three directions, with no principle axis aligned in a vertical or horizontal direction. In this situation, various approaches have been developed for measuring anisotropy using packer tests in multiple holes. The *dipole flow test*, recently described by Kabala (1993/T7.5), is a single-hole, multilevel packer test that measures distribution of horizontal and vertical hydraulic conductivity and the specific storativity when applied to different bounded intervals. Table 7.6 provides an index to references where more detailed information on specific methods for measuring anisotropy can be obtained.

7.5.3 Presence and Degree of Confinement

The presence and degree of confinement has a significant impact on the vulnerability of an aquifer to contamination and the size of the WHPA for a given time of travel or drawdown criterion (Section 11.2.1). Figure 7.12 shows the location of major and significant minor confined aquifers in the contiguous U.S. Methods for evaluating these aquifer properties can be broadly classified as (1) geologic, (2) hydrologic, and (3) hydrochemical. Table 7.4 identifies 15 indicators of confinement and the characteristics that are associated with highly confined or semiconfined conditions. Kreitler and Senger (1991)²⁷ provide more detailed discussion of these methods.

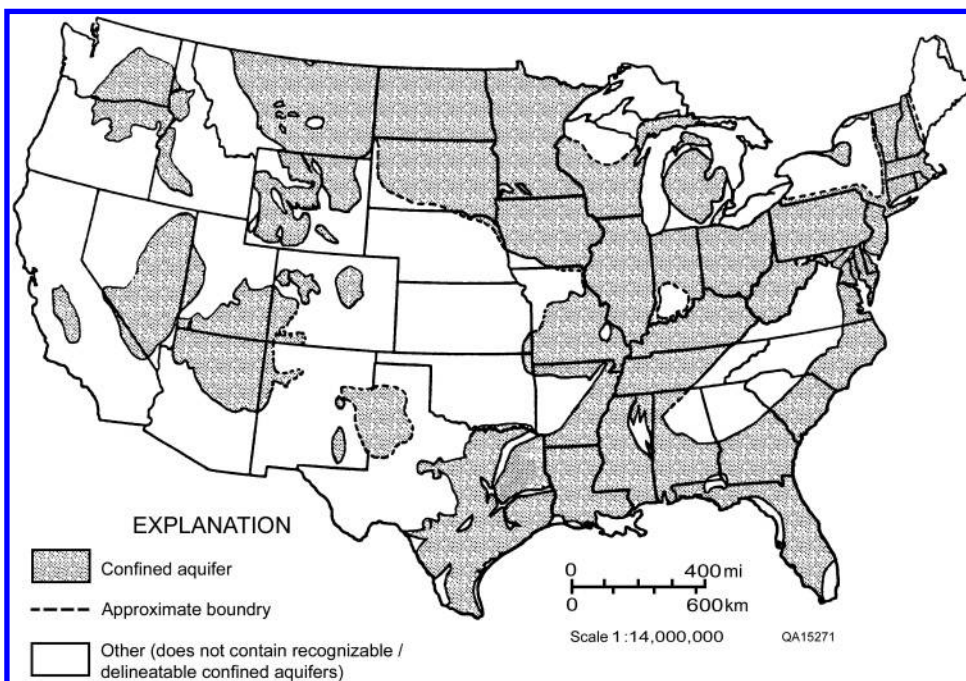


Figure 7.12 Major and significant minor confined aquifers of the U.S. (Kreitler and Senger, 1991).

²⁷ Kreitler, C.W. and R.K. Senger. 1991. Wellhead Protection Strategies for Confined-Aquifer Settings. EPA/570/9-91-008, 168 pp.

Table 7.4 Indicators of Presence and Degree of Confinement

Information Source	Highly Confined	Semiconfined (Leaky)
Geologic		
Geologic maps and cross sections	Presence of continuous, unfractured, confining strata (clays, glacial till, shale, siltstone)	Evidence of vertical permeability in confining strata (fracture traces, faults, mineralization or oxidation of fractures observed in cores)
Environmental geologic and hydrogeologic maps	See above	Presence of artificial penetrations (abandoned or producing oil and gas wells, water wells, exploration boreholes)
Hydrologic		
Water level elevation (single well) of potentiometric surface	Above the top of the aquifer (not diagnostic for differentiation of highly and semiconfined aquifers)	Same
Hydraulic head differences between aquifers	Large head difference in water levels measured in wells cased in different aquifers (not diagnostic for differentiation of highly and semiconfined aquifers)	Same
Water level fluctuations (continuous measurement)	Short-lived and diurnal fluctuations in response to changes in barometric pressure, tidal effects, external loading (Table 2.2); no response to recharge events	Similar to highly confined aquifer, but may also exhibit relatively large and rapid response to recharge events because of leakage through discrete points
Hydrologic measurements in confining strata	No changes in water levels in response to pumping; diurnal but not seasonal water level fluctuations (see above)	Changes in water levels in response to pumping; seasonal water level fluctuations in response to seasonal variations in precipitation
Aquifer test for storativity	Storativity less than 0.001	Between 0.01 and 0.001 (not diagnostic)
Aquifer test for leakage	Pump drawdown vs. time curve matches analytical solution(s) for highly confined aquifer; estimated or calculated leakage less than 10^{-3} gal/day/ft ²	Pump drawdown vs. time curve requires use of analytical solution for leaky aquifer; estimated or calculated leakage 10^{-2} to 10^2 gal/day/ft ²
Numerical modeling	Simulation of potentiometric surface possible without estimates of leakage, or required estimates are low (see above)	Simulation of potentiometric surface requires use of large leakage values
Hydrochemistry		
General water chemistry	Chemical characteristics indicative of long distance from recharge area (region specific)	Qualifies as confined using other criteria, but chemical characteristics more similar to ground water in recharge zones
Anthropogenic atmospheric tracers	No detectable tritium or fluorocarbons in ground water	Detectable concentrations of tritium or fluorocarbons (less than 40 years old)
Isotope chemistry	Carbon-14 dating of water samples indicates age of >500 years	See above
Contaminants	No detectable concentrations of potential contaminants identified by inventory of potential contaminant sources	Qualifies as confined using other criteria, and contaminants detected in aquifer
Changes in water chemistry over time	Head declines from long-term pumping have not resulted in changes in water chemistry indicators of vertical leakage	Head declines from long-term pumping have resulted in changes in water chemistry indicators of vertical leakage (see above)
Time of travel through confining strata	Time-of-travel calculations based on measured or estimated values of difference in hydraulic head, porosity, and hydraulic conductivity exceed 40 years	Time of travel through confining strata less than 40 years based on calculations or presence of tritium or fluorocarbons

Source: Adapted from Kreitler and Senger (1991).

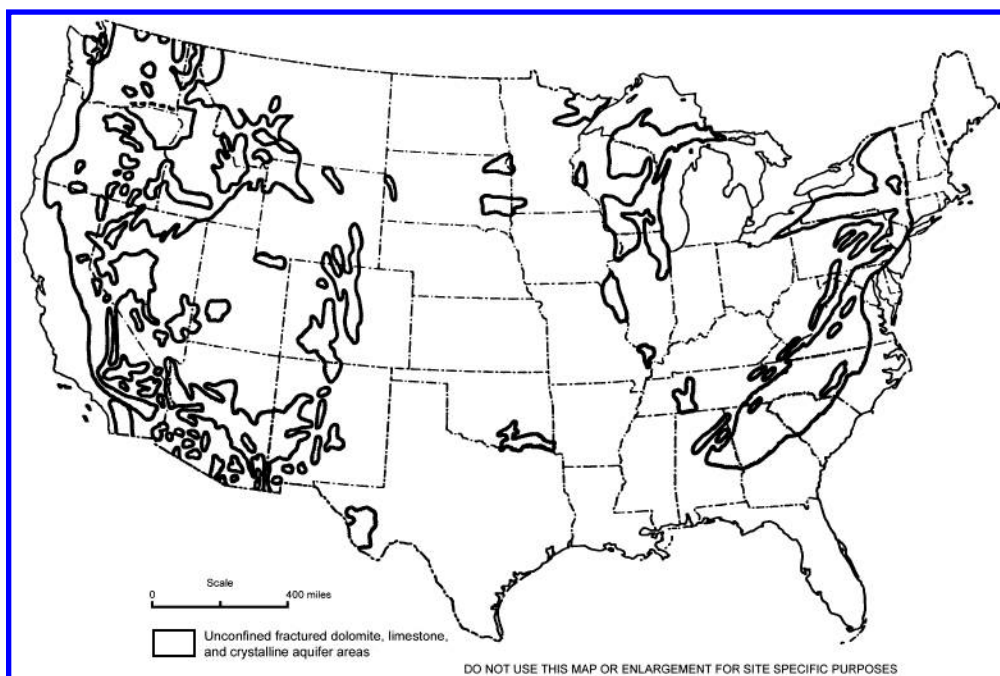


Figure 7.13 Major areas of unconfined fracture rock aquifers in the U.S. (Bradbury et al., 1991).

7.5.4 Characterization of Fractured Rock and Karst Aquifers

Where fracture or conduit flow (Section 2.5.4) occurs in an aquifer, special care and techniques are required for delineating wellhead protection areas. Figure 7.13 identifies major areas of the U.S. and associated territories where unconfined fracture flow is significant, and Figure 1.10 identifies major karst areas of the contiguous U.S. and other areas where carbonate rocks are at or near the surface. The term *fractured rock* aquifer in this book refers to areas where most of the water supplied to a pumping well comes from fractures with sufficiently narrow apertures that Darcian flow (Section 2.6.3) occurs. Common geologic settings where fractured rock aquifers occur include crystalline intrusive igneous (i.e., granites) and metamorphic rocks, basalts, and some carbonates.

The term *karst* aquifer in this book refers to carbonate aquifers where conduit flow is an important component of the ground-water flow system. Generally, where apertures are >5 mm in diameter or width and water velocity is >0.001 m/sec, ground-water flow is turbulent rather than Darcian. As shown in Figure 1.10, not all carbonate rocks (limestone and dolomite) are karst aquifers. However, whenever carbonate aquifers are present, either fracture or conduit flow should be assumed.

The fundamental objective of hydrogeologic mapping in fractured rock and karst aquifers should be to identify (1) the *boundaries* of the flow system, and (2) the *structure* of the flow system. Important elements in defining the structure of a carbonate aquifer include (1) relative importance of diffuse and conduit flow, (2) the amount of storage in soil above the aquifer, and 3) the extent to which recharge comes from point sources, such as sinkholes, or is dispersed. The rest of this section provides an overview of major methods for characterizing the boundaries and structure of fracture rock and karst systems. Table 1.4 provides an extensive list of major references on karst geology, geomorphology, and hydrology where more detailed information can be obtained.

The primary method for mapping the boundaries of an unconfined fractured rock or karst aquifer is dye tracing (Section 8.4). In karst aquifers this is the *only* reliable method because conduit flow systems often do not follow surface water drainage systems. For example, Bonacci and

Živaljević (1993),²⁸ using dye tracing and a water budget of a large spring in the Dinaric karst of Montenegro, found the catchment area to be 76 to 79 km², while hydrogeologic mapping based on geology and topography indicated a catchment area of 120 to 170 km².²⁹

Significant differences in flow direction may occur in karst aquifers depending on whether low-flow or high-flow conditions exist. Again, such changes can only be accurately determined using properly designed dye tracer tests. For example, low-flow and high-flow tracer tests were conducted by injecting dye into several wells in the vicinity of Lemon Lane landfill, a Superfund site contaminated with PCBs (McCann and Krothe, 1992).³⁰ The landfill is located on a topographic divide in a karst area where more than 30 springs have been identified within a mile-and-a-half radius of the landfill. A low-flow tracer test conducted in 1987 found that most water infiltrating in the vicinity of the landfill flowed in a southeasterly direction, but some also flowed to the northeast. A high-flow tracer test, conducted 2 years later, found that most flow was still in a southeasterly direction, but that some flow occurred in all directions, with dye being detected in springs up to a mile and a half distant in all directions from the landfill.

A variety of methods are available for characterizing the structure of fractured rock and karst flow systems. These can be broadly classified as (1) remote sensing, surface, and borehole geophysical methods; (2) monitoring of natural fluctuations of water levels in wells and their response to pumping; and (3) monitoring of discharge and chemistry of springs.

Remote Sensing and Geophysical Methods. Fracture-trace and lineament analysis using air photos is a useful starting point for identifying possible areas of concentration and preferential direction of ground-water flow.³¹ Other remote sensing methods, such as near-infrared and thermal infrared scanners, which detect variations in near-surface moisture, may also be useful for mapping the location of sinkholes and fracture-trace analysis (LaMoreaux, 1979).³² Such observations should be supplemented, where possible, with observation and analysis of the character and orientation of rock joint and fracture patterns at surface outcrops (LaPointe and Hudson, 1985).³³

A number of commonly used surface geophysical methods have potential applications for detection of shallow subsurface cavities in karst areas, including gravity, electrical resistivity, seismic, and ground-penetrating radar (Greenfield, 1979).³⁴ Karous and Mareš (1988)³⁵ provide detailed treatment of use of geophysical methods for characterizing fractured rock aquifers, including some methods that are less commonly known. For example, [Figure 7.14](#) illustrates how a conduit feeding a karst spring can be mapped using self-potential measurements. In this example, the current electrode A was grounded at the spring orifice, and potentials measured along transects I through IV. In the U.S., natural potential (another term for self-potential) has been used in karst areas for siting of monitoring wells, delineation of flow paths, mapping of drawdown recovery patterns associated with pumping, and minimizing effects of petroleum drilling (Lange and Kilty, 1992).³⁶

²⁸ Bonacci, O. and R. Živaljević. 1993. Hydrological Explanation of the Flow in Karst: Example of the Crnojevića Spring. *Journal of Hydrology* 146:405–419.

²⁹ Note that the hydrogeology of karst terranes of the former Yugoslavia is generally very different from karst areas in North America. In the U.S., catchments in karst areas typically are larger than would be expected based on an analysis of surface topography.

³⁰ McCann, M.R. and N.C. Krothe. 1992. Development of a Monitoring Program at a Superfund Site in a Karst Terrane Near Bloomington, Indiana. *Ground Water Management* 10:349–370. [Proceedings of the 3rd Conference on Hydrogeology, Ecology, Monitoring and Management of Ground Water in Karst Terranes]

³¹ Fracture-trace analysis will not necessarily identify major conduits in karst aquifers, however, because these may follow bedding planes with no surface expression.

³² LaMoreaux, P.E. 1979. Remote-Sensing Techniques and the Detection of Karst. *Association of Engineering Geologists Bulletin* 16(3):383–392.

³³ LaPointe, P.R. and J.A. Hudson. 1985. Characterization and Interpretation of Rock Mass Joint Patterns. *Geological Society of America Special Paper* 199, Boulder, CO, 37 pp.

³⁴ Greenfield, R.J. 1979. Review of Geophysical Approaches to Detection of Karst. *Association of Engineering Geologists Bulletin* 16(3):398–408.

³⁵ Karous, M. and S. Mareš. 1988. *Geophysical Methods in Studying Fracture Aquifers*. Charles University, Prague, 93 pp.

³⁶ Lange, A.L. and K.T. Kilty. 1992. Natural-Potential Responses of Karst Systems at the Ground Surface. *Ground Water Management* 10:179–193. [Proceedings of the 3rd Conference of Hydrogeology, Ecology, Monitoring and Management of Ground Water in Karst Terranes]

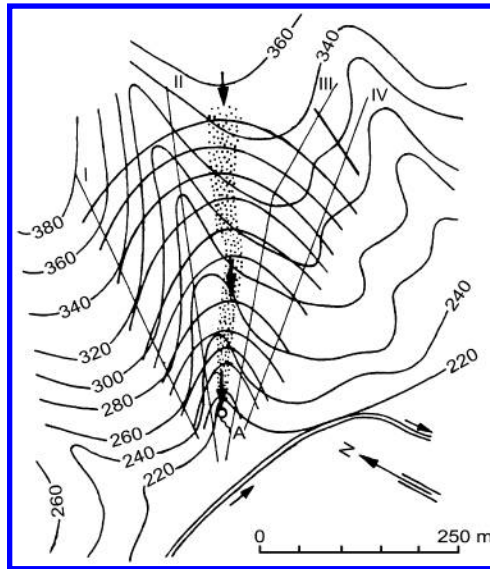


Figure 7.14 Mapping of subsurface conduit using self-potential method (Karous and Mareš, 1988).

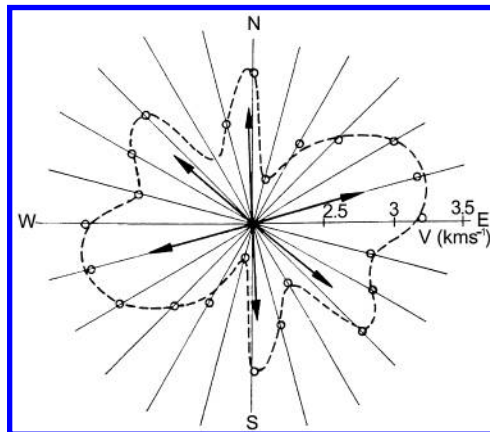


Figure 7.15 Azimuthal seismic survey to characterize direction of subsurface rock fractures (Karous and Mareš, 1988).

Figure 7.15 illustrates how repeated seismic velocity measurements at different orientations around a single point provide an indication of the orientation of major fractures. In this example, velocities have been plotted on a polar diagram, with the inferred direction of major fractures based on the higher velocity measurements. Azimuthal resistivity, in which a series of resistivity measurements are taken by shifting the position of the electrodes around a single point, is another possible method for detecting fracture orientation (Ritzi and Andolesk, 1992).³⁷ Azimuthal methods may be useful for identifying fracture zones that contribute to recharge of karst systems, but may not be successful in locating zone of conduit flow, which tends to be along bedding planes, often without any surface expression as fracture traces.

Borehole geophysical methods provide a necessary complement to surface geophysical and other characterization techniques (Section 6.4). Acoustic viewer, borehole television, and dip-meter logs are especially useful for determining the location and orientation of subsurface fractures.

³⁷ Ritzi, R.W., Jr. and R.H. Andolesk. 1992. Relation between Anisotropic Transmissivity and Azimuthal Resistivity Surveys in Shallow, Fractured, Carbonate Flow Systems. *Ground Water* 30(5):774–780.

Fracture zones can also be detected using borehole flowmeters (mechanical, thermal, and the recently developed electromagnetic flowmeter) with or without pumping. Single-borehole and multiple-well tracer tests are useful for characterizing the flow at a more local scale. Table 7.6 identifies a number of additional references characterizing fractured rock aquifers.

The U.S. Geological Survey has developed a multidisciplinary “toolbox” approach to characterize ground-water flow in contaminated fractured rock.³⁸ The approach integrates surface and borehole geophysical methods, special measures to prevent cross contamination, tracer and other hydrologic testing, discrete interval completions based on fracture network characterization, and chemical sampling. Table 7.6 identifies a number of references that illustrate surface and borehole techniques used in the toolbox.

Water Level Monitoring. In unconfined fractured rock and karst aquifers, water levels in wells intercepting fractures or conduits commonly show relatively large fluctuations in response to precipitation events (see Figure 1.9). During times of low flow, large differences in water levels in nearby wells serve as an indicator of low matrix permeability (the well with higher water levels) and fracture or conduit flow in the well with the lower water levels.

The response of water levels to pumping provides a basis for judging whether the flow system functions as a porous medium equivalent (i.e., the aquifer can be modeled as if it were flowing in a porous medium, even though flow in fractures is occurring).³⁹ Figure 7.16 illustrates three types of aquifer responses to pumping that indicate a porous medium model should *not* be used for characterizing an aquifer. The left-hand side of Figure 7.16 illustrates three types of aquifer responses that are indicative of a porous medium equivalent, and the right-hand side indicates aquifers where large fracture or conduit flow is present. Granular aquifers (and fractured rock aquifers where fractures are relatively small and evenly spaced) will generally show a linear relationship between drawdown and pumping rate, whereas aquifers where fracture flow is significant may show a leveling-off response in drawdown as pumping rates increase (Figure 7.16a). The presence of large water-bearing fractures is indicated by a temporary leveling off in a drawdown vs. time plot (Figure 7.16b). Finally, if major fractures are feeding a well, the cone of depression may depart significantly from a circular or elliptical shape (Figure 7.16c). Nonporous medium equivalent responses in aquifer tests require use of the appropriate fracture-flow analytical solutions for analyzing pump test data (Table 7.6). All these responses can also be indicative of conduit flow in carbonate aquifers.

Spring Monitoring. A distinctive characteristic of near-surface karst hydrologic systems is that springs serve as discharge points for subsurface flow. Much useful information about a karst aquifer can be obtained by monitoring the amount and chemistry of flow from a spring. Kresic (1993)⁴⁰ provides a review of methods for spring hydrograph analysis and statistical analysis of time-series measurements of flow from springs and water level measurements in wells. With antecedent soil moisture conditions being equal, a rapid increase in discharge from a spring in response to a precipitation event indicates that point recharge is a major component of subsurface flow, whereas a relatively small flow response indicates that dispersed recharge contributes most of the flow to a spring. Quantitative interpretations of spring hydrographs require continuous records of both spring

³⁸ Haeni, F.P., J.W. Lane, Jr., J.H. Williams, and C.D. Johnson. 2001. Use of a Geophysical Toolbox to Characterize Ground-Water Flow in Fractured Rock. In: Fractured Rock 2001 Conference Proceedings, Toronto, Ontario, March 26–28, 2001, CD-ROM.

³⁹ In the context of wellhead protection, even if a fractured rock or karst aquifer can be modeled using porous medium flow assumptions, results should be interpreted with great caution. Values of hydraulic conductivity calculated from such aquifer tests will reflect average values, whereas actual ground-water flow velocities will be much higher. For example, Quinlan et al. (1992 — footnote 41) cite a tracer test in the Floridan aquifer using two wells 200 ft apart. The theoretical arrival time of the injected dye, based on geophysical logging and aquifer testing, was about 40 days. Actual breakthrough time was 5 h.

⁴⁰ Kresic, N.A. 1993. Review and Selected Bibliography on Quantitative Definition of Karst Hydrogeological Systems. In: Annotated Bibliography of Karst Terranes, Vol. 5, with three review articles, P.E. LaMoreaux, F.A. Assaad, and A. McCarley (eds.), International Contributions to Hydrogeology, Vol. 14, International Association of Hydrogeologists, Verlag Heinz Heise, Hannover, West Germany, pp. 51–87.

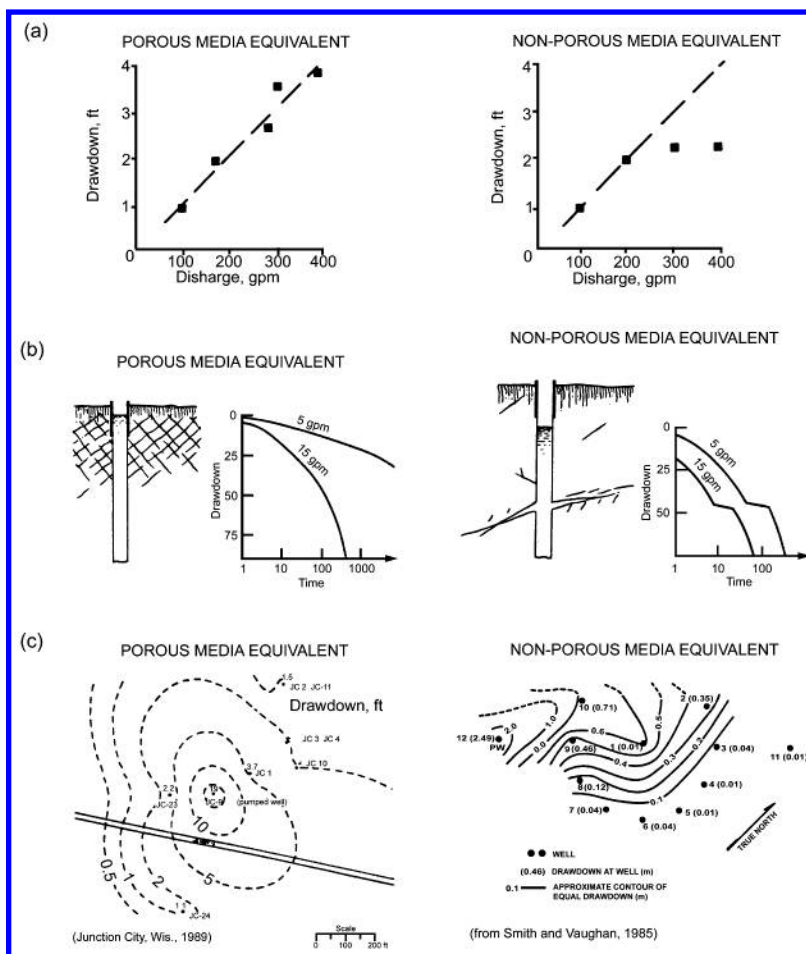


Figure 7.16 Pumping-test response indicators of fracture/conduit flow: (a) discharge drawdown plots; (b) time drawdown curves; (c) areal drawdown distribution (Bradbury et al., 1991).

discharge and precipitation in the catchment area (which must be delineated by properly designed tracer testing).

Specific conductance, an easily measured ground-water parameter, is widely used for characterizing karst aquifers. Where multiple springs are present in an area, springs with similar specific conductance can be considered to be closely interconnected, while large differences in specific conductance indicate that the flow systems feeding the springs are largely independent. Monitoring of changes in water chemistry with changes in spring discharge is also a useful way to characterize karst aquifers. Specific conductance is the parameter of choice because it is easy to measure and can be monitored continuously (Quinlan et al., 1992).⁴¹ Other parameters such as hardness, degree of saturation with respect to calcite and dolomite, and the Ca/Mg ratio can also be used. A high coefficient of variation of specific conductance (CVC) indicates that point recharge is a major contributor to flow, whereas a low CVC indicates that most recharge comes from dispersed sources. Quinlan et al. (1992 — footnote 41) suggest the following provisional guidelines using CVC as a

⁴¹ Quinlan, J.F., P.L. Smart, G.M. Schindel, E.C. Alexander, Jr., A.J. Edwards, and A.R. Smith. 1992. Recommended Administrative/Regulatory Definition of Karst Aquifer, Principles for Classification and Carbonate Aquifers, Practical Evaluation of Vulnerability of Karst Aquifers, and Determination of Optimum Sampling Frequency at Springs. Ground Water Management 10:573–635. [Proceedings of the 3rd Conference on Hydrogeology, Ecology, Monitoring and Management of Ground Water in Karst Terranes]

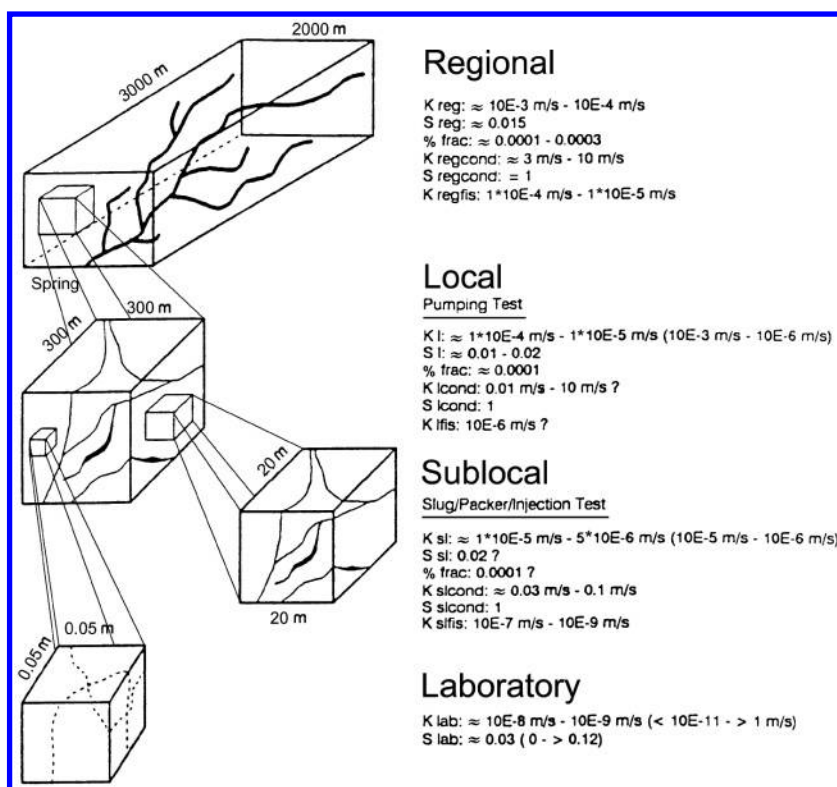


Figure 7.17 Geometrical relationships and hydraulic conductivities at different scales in karst systems (Sauter, 1992).

measure of aquifer vulnerability: moderately sensitive = <5%, very sensitive = 5 to 10%, hyper-sensitive = >10%.

A Cautionary Note. Footnote 39 discussed the possible risk of using porous medium analytical models for delineating WHPAs in fractured rock or karst areas, even if aquifer test data suggest that flow behavior approximates that in a porous medium. The results of any methods used to quantify storage properties or hydraulic conductivity in fractured rock and karst aquifers described above must be evaluated in the context of the volume of the aquifer that is being measured. As noted in [Section 7.3.4](#), values for hydraulic conductivity tend to increase as larger volumes of an aquifer are measured. This effect is particularly dramatic in karst aquifers. Figure 7.17 shows the effect of scale from laboratory core measurements (centimeters) to regional (thousands of meters) on the storage coefficient (S) and hydraulic conductivity (K) in the Swabian Alps of southwestern Germany. Measurements of K range over six orders of magnitude. [Figure 7.18](#), which summarizes data from many different studies in karst areas, shows an even wider range of eight orders of magnitude for the *predominant* ranges of major methods for estimating average velocity (laboratory core, double-packer tests, slug tests, aquifer pump tests, and dye tracer tests). These figures make it clear that time-of-travel estimates used for delineation of wellhead protection areas in karst aquifers based on any methods other than dye tracer tests are unlikely to provide adequate protection.

7.6 GUIDE TO MAJOR REFERENCES

[Table 7.5](#) identifies major references on vadose zone and ground-water hydrologic characterization covering the following major topics: (1) vadose zone hydrology (unsaturated hydraulic

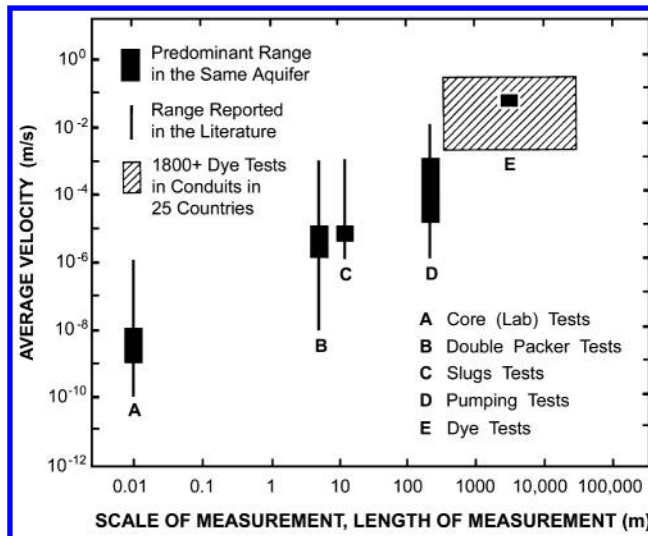


Figure 7.18 Measurement scales and average velocities of different measurement methods (modified after Quinlan et al., 1992, and Sauter, 1992).

conductivity and saturated hydraulic conductivity above a water table), (2) aquifer tests (shallow water table tests, slug tests, packer tests, and multiple-well pump tests), and (3) water balance methods. Dawson and Istok (1991) and Kruseman and de Ridder (1991) are good references on design and analysis of aquifer tests. Butler (1997) is the best single reference on the use of slug tests. Most of the vadose zone hydrology and hydrogeology texts identified in Table 2.4 also cover field measurement methods. Methods for conducting and analyzing slug and packer tests are a relatively active area of research and development, so Table 7.5 contains a higher portion of journal citations than most of the reference tables in this book.

Table 7.6 provides an index of more than 120 source references covering (1) specific pump test analytical solutions for a variety of aquifer conditions, (2) methods for measuring anisotropy, and (3) methods for characterizing fractured rock. References indexed in this table are almost exclusively from the journal literature and stand as an exception to the practice in this book of focusing on major texts and references. The first part of this table can be used with Worksheet D-W4 to identify the source literature on analytical solutions where hydrogeologic and well characteristics make use of the Theis and Jacob's solutions inappropriate (see Section 7.3.2 for the basic assumptions).

In this chapter and elsewhere in this book, the importance of considering the effect of anisotropy and fracture flow in ground-water systems has been emphasized. Table 7.6 also provides an index to the literature on these topics, which tend to not be addressed comprehensively in other sources.

Table 7.5 Index to Major References on Hydraulic Conductivity and Water Balance Test Methods

Topic	References
Vadose Zone Hydrology (see also Table 2.4)	
Unsaturated	<u>Hydraulic Conductivity</u> : ASTM (D6527/TA.14), Boulding (1993), Bouma (1977), Bouma et al. (1974), Bouwer and Jackson (1974), Dirksen (1991), Green et al. (1986), Hendrickx (1990), Hillel and Benyamini (1974), U.S. EPA (1986), van Genuchten et al. (1989); <u>Air Permeability</u> : ASTM (D6539/TA.14), Springer et al. (1998-SAP/CMP)
Saturated (Above Water Table)	Amoozegar and Warrick (1986), Boersma (1965), Boulding (1993), Bouwer and Jackson (1974), Freifeld and Oldenburg (2000 — restricted interval Guelph permeameter), Hamilton et al. (1981), Hendrickx (1990), Kessler and Oosterbaan (1974), Lambe (1955), Stephens and Neuman (1980, 1982a, 1982b, 1982c), Sai and Anderson (1991), Stephens et al. (1988), Winger (1960), Youngs (1991), Zhang et al. (1999 — concentric-disk tension infiltrometer); <u>Method Comparisons</u> : Havlena and Stephens (1992), Lee et al. (1985), Reynolds et al. (1983), Roberts (1984), Sai and Anderson (1991), U.S. EPA (1986)
Aquifer Tests (see ASTM (1999) for compilation of relevant standards)	
Shallow Water Table Tests	Amoozegar and Warrick (1986), Boersma (1965), Boulding (1993), Bouma (1979, 1983), Bouwer and Jackson (1974), Johnson and Richter (1967), Kessler and Oosterbaan (1974), Luthin (1957), Schmid (1967), U.S. EPA (1986), Youngs (1991)
Slug Tests ^a	<u>Texts/Reviews</u> : Bentall (1963a), Butler (1997), Campbell et al. (1990), Chapus (1989), Chirlin (1990), Dagan (1978), Dawson and Istok (1991), Herzog and Morse (1990), Kraemer et al. (1990), Leap (1984 — method comparisons), Olson and Daniel (1981), Sevee (1991), Wynne (1992); <u>Pressure Displacement</u> : Leap (1984), Levy and Pannell (1991), McLane et al. (1990), Orient et al. (1987), Prosser (1981); <u>Multilevel Tests</u> : Butler et al. (2002), Mastrodonardo and Thomsen (1992), Melville et al. (1991), Molz et al. (1990a, 1990b), Scaturro and Widdowson (1997), Widdowson et al. (1989, 1990); <u>Hvorslev Method</u> : Chirlin (1989), Hvorslev (1951); <u>Ferris-Knowles Method</u> : Ferris and Knowles (1954, 1963), Ferris et al. (1962); <u>Cooper-Bredehoeft-Papadopoulos Method</u> : Cooper et al. (1967), Papadopoulos et al. (1973); <u>Bouwer-Rice Method</u> : Bouwer (1989), Bouwer and Rice (1976); <u>Fissured Aquifers</u> : See Table 7.6; <u>Measurement Volume</u> : Guyonnet et al. (1993); <u>Data Analysis Procedures</u> : Dax (1987), Faust and Mercer (1984), Karasaki and Witherspoon (1988), Keller and van der Kamp (1992), Marschall and Barczewski (1989), Moench and Hsieh (1985), Nguyen and Pinder (1984), Novakowski (1989), Palmer and Paul (1987), Peres et al. (1989), Sageev (1986), Widdowson et al. (1990)
Packer Tests	Braester and Thunvik (1984), Brassington and Walthall (1985), Bredehoeft and Papadopoulos (1980), Dagan (1978), Koopman et al. (1962), Sevee (1991), Shuter and Pemberton (1978), Sutcliffe and Joyner (1966); <u>Dipole Flow Test</u> : Kabala (1993), Zlotnick and Zurbuchen (1998); <u>Lugeon Test</u> : Houlsby (1976), Pearson and Money (1977), Roeper et al. (1992); see also references for multilevel slug tests
Pumping Tests ^a	Bedinger and Reed (1988), Bentall (1963a, 1963b), Bruin and Hudson (1955), Clarke (1988), Dawson and Istok (1991), Earlougher (1977), Ferris et al. (1962), Johnson and Richter (1966), Kruseman and de Ridder (1990), Lebbes (1999), Osborne (1993), Schicht (1972), Stallman (1971), Streltsova (1989), U.S. EPA (1986, 1991), U.S. Geological Survey (1980), van Haveren (1986), Walton (1962, 1979, 1987), Wenzel (1942); see also Table 7.6 for references on analytical solutions
Other Tests	<u>Direct-Push Methods</u> : Butler et al. (2000), Scaturro and Widdowson (1997); <u>Hydraulic Tomography</u> : Yeh and Liu (2000); <u>In Situ Permeable Flow Sensor</u> : Alden and Munster (1997), Ballard (1996), Ballard et al. (1996); <u>Precision Temperature Logs</u> : Reiter (2001)
Waste/Waste Transport	Conrad et al. (1993), Daniel and Trautwein (1994)

Table 7.5 Index to Major References on Hydraulic Conductivity and Water Balance Test Methods (*Continued*)

Topic	References
Water Balance Methods	
Texts/Reviews	Boulding (1993), Chapman (1964), Downes (1964), Hagan et al. (1967), Meinzer (1932), Phillips (1964, 1969), Rijtema and Wassink (1969), Sokolow and Chapman (1974), Thornthwaite and Mather (1955, 1957). The following references identified in Table 2.4 have sections on water balance methods: ASCE (1952), Brown et al. (1983), Bureau of Reclamation (1981), Childs (1969), Dunne and Leopold (1978), Skeat (1969), Walton (1970)
Aquifer Recharge	Andres (1991), Keefer and Berg (1990), Louie et al. (2000 — passive capillary samplers), Rehm et al. (1982)
Stormwater Infiltration	Ferguson (1994)

^a Most basic hydrogeology and hydraulics texts (Table 2.4) also cover pump test and slug tests. Texts in this table commonly cited in relation to pump test analysis include Bureau of Reclamation (1981), Freeze and Cherry (1979), Lohman (1972), and Driscoll (1986).

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* See Preface for information on how to obtain documents from CERl and NTIS.

Table 7.6 Index to Source References on Pump Test Analytical Solutions and Methods for Characterizing Anisotropic and Fractured Rock Aquifers

Topic	References
General	Bruggeman (1999)
	Pump Test Solutions: Confined Aquifers^a
Nonleaky	Fully Penetrating Wells — Constant Discharge: Cooper and Jacob (1946), Jacob (1950), Theis (1935); Variable Discharge: Abu-Zied and Scott (1963), Aron and Scott (1965), Hantush (1964), Lai et al. (1973), Moench (1971), Stallman (1962); Constant Drawdown: Hantush (1964), Jacob and Lohman (1952), Rushton and Rathod (1980); Unclassified: Boulton and Streltsova (1977a, 1977b), ^b Brutsaert and Corapcioglu (1976), Moench and Prickett (1972), Papadopoulos (1967), Reed (1980); Partially Penetrating Wells — Hantush (1961a, 1964)
Leaky, fully penetrating wells	No Storage in Confining Bed: Hantush and Jacob (1955); Storage in Confining Bed: Hantush (1960); Multiple Aquifers: Hantush (1967a), Neuman and Witherspoon (1972); Unclassified: Corapcioglu (1976), Hantush (1956, 1959, 1964, ^b 1967b), Jacob (1946a), Lai and Su (1974), Neuman and Witherspoon (1969b), Reed (1980)
	Pump Test Solutions: Unconfined Aquifers^a
Fully penetrating wells	Constant Discharge: Boulton (1954a, 1954b, 1963), Neuman (1972, 1973); Unclassified: Boulton and Streltsova (1978), ^b Cooper and Jacob (1946), Jacob (1944, 1963), Neuman (1975), ^b Prickett (1965), Streltsova (1972); Vadose Zone Effects: Guitjens and Luthin (1971), Krozynski and Dagan (1975)
Partially penetrating wells	Boulton and Streltsova (1976), ^b Hantush (1961a, 1962), Neuman (1974), Streltsova (1974, ^b 1976a ^b)
	Tests for Special Aquifer Conditions
Test Analysis	Single-Well Step-Drawdown Tests: Bierschenk (1964), Jacob (1946b), Lennox (1966), Rorabaugh (1953); Multiple Aquifers: Aral (1990a, 1990b), Bennett and Patton (1962), Hantush (1967a), Javendal and Witherspoon (1969), Neuman and Witherspoon (1969a — confined, 1972 — leaky)
Other Conditions	Aquitard/Aquiclude Hydraulic Conductivity: Neuman and Gardner (1989); Lateral Boundary: Ferris et al. (1962), Lohman (1972), Stallman (1963)
Other	Contaminant Transport: Mills et al. (1985); Large-Diameter Well: Papadopoulos and Cooper (1967); Unclassified: Boulton and Streltsova (1975)
	Anisotropy
General	Bear and Dagan (1965), Fetter (1981), Freeze (1975), Greenkorn (1970), Liakopoulos (1965), Maasland (1957a, 1957b, 1983), Marcus (1962), Scheidegger (1954)
Pump Test Methods ^c	Cited by ASTM D4043: Hantush (1961b), Neuman (1975), Papadopoulos (1965), Weeks (1964, 1969); Other Citations: Boulton and Streltsova (1976, 1977a, 1977b, 1978), Butler and Liu (1993), Dagan (1967), Hantush (1964, 1966a, 1966b), Hantush and Thomas (1966), Hsieh and Neuman (1985), Mansur and Dietrich (1965), Neuman (1975), Neuman et al. (1984), Norris and Fidler (1966), Streltsova (1974, 1976a), Way and McKee (1982)
Other Methods	Laboratory Methods: Banton (1993), Rocha and Franciss (1977); Other Field: Loo et al. (1984 — surface tiltmeter survey), Maasland (1955 — auger hole method), Ritzi and Andolesk (1992 — azimuthal resistivity)

Table 7.6 Index to Source References on Pump Test Analytical Solutions and Methods for Characterizing Anisotropic and Fractured Rock Aquifers (*Continued*)

Topic	References
Fractured Rock Characterization	
General	Bianchi and Snow (1968), Chen (1989), Committee on Fractured Rock Characterization and Flow (1996), Duguid and Lee (1977), Faybishenko et al. (2000), Gale (1982), Gerke and van Genuchten (1993), Long and Billaux (1987), Long and Witherspoon (1985), Long et al. (1982), Nelson (1985), Neuman and Neretnieks (1990), NRC (2001 — fractured vadose zone), Sagar and Runchai (1982), Schmelling and Ross (1989), Singhal and Gupta (1999), Snow (1969), Streltsova (1976b), Thomas and McGlew (1985), Tsang (1992), Tsang and Tsang (1987), UNESCO (1984), Warren and Root (1973); <u>DNAPLs</u> : Schuille (1998), U.S. EPA (2001)
USGS Toolbox Approach	<u>General</u> : Haeni et al. (2001), Shapiro et al. (1999); <u>Case Studies</u> : Johnson et al. (2002a, 2002b — Storrs, CT), Lane et al. (2001, 2002 — Norwalk, CT), Powers et al. (1999 — Storrs, CT), Williams and Paillet (2002 — Watervliet Arsenal, NY), Williams et al. (2002 — Ventura County, CA)
Well Test Methods	<u>Cited by ASTM D4043</u> : Barenblatt et al. (1960), Boulton and Streltsova (1977b), Gringarten and Ramey (1974), Moench (1984); <u>Other Citations</u> : Boulton and Streltsova (1977a, 1978), Elkins and Skov (1960), Gale (1982), Gringarten (1982), Gringarten and Witherspoon (1972), Hsieh and Neuman (1985), Hsieh et al. (1983, 1985), Huntley et al. (1992), Jenkins and Prentice (1982), Lewis (1974), Maslia and Randolph (1987), McConnel (1993), Moore (1992), Ramey (1975), Rofail (1967), Sauveplane (1984), Smith and Vaughn (1985), Zekai (1986); <u>Ground-Penetrating Radar</u> : Tsolias et al. (2001); <u>Slug Tests</u> : Barker and Black (1983); <u>Tracers</u> : Lewis et al. (1966).

^a Categories in first column taken from Driscoll (1986); subcategories in the second column taken from ASTM D4043 (full citation in Table A.14). Unclassified references are identified in Driscoll (1986) and other sources, but not ASTM D4043.

^b Analytical solutions for anisotropic aquifer conditions.

^c See also references for pump test methods in fractured rock, which also characterize anisotropy, when present.

Table 7.6 References (Appendix F contains references for figure and table sources.)

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Soil and Ground Water Tracers

In hydrogeology, the term *tracer* refers to distinguishable matter or energy carried by ground water that gives information concerning the ground-water system. A tracer can be entirely natural, such as the heat carried by hot spring waters; it can be accidentally introduced, such as fuel oil from a ruptured storage tank; or it can be introduced intentionally, such as dyes placed in water flowing within limestone caves.

This chapter examines the use of tracers in hydrogeology with special emphasis on the study of contaminant behavior. Section 8.1 discusses the types and uses of tracer tests, Section 8.2 discusses the factors that should be considered in selecting a tracer, and Section 8.3 describes the general characteristics of major types of tracers. The chapter concludes with an examination of methods for tracing in karst systems (Section 8.4) and porous media (Section 8.5).

8.1 TYPES AND USES OF TRACER TESTS

The variety of tracer tests is almost infinite, considering the various combinations of tracer types, local hydrologic conditions, injection methods, sampling methods, and geological settings. Tracer tests are used for two main purposes: (1) to measure one or more hydrogeologic parameters of an aquifer, and (2) to identify sources, velocity, and direction of movement of contaminants. Tracer tests can also be broadly classified according to whether they rely on natural gradient flow or induced flow by pumping or some other means. Quinlan et al. (1988)¹ discuss how to recognize false negative and false positive tracer results.

8.1.1 Measurement of Hydrogeologic Parameters

Tracers can be used to measure or estimate a wide variety of hydrogeologic parameters, most commonly direction and velocity of flow and dispersion. Depending on the type of test and the hydrogeologic conditions, other parameters such as hydraulic conductivity, porosity, chemical distribution coefficients, source of recharge, and age of ground water can be measured.

Figure 8.1 shows six examples of tracer measurement of hydrogeologic characteristics by natural gradient flow. Figure 8.1a shows the measurement of flow velocity in a cave system, and Figure 8.1b shows the use of a tracer to check subsurface flow patterns in a karst area with sinking and rising streams. The use of a tracer to measure the velocity of movement of dissolved material

¹ Quinlan, J.F., R.O. Ewars, and M.S. Field. 1988. How to Use Ground-Water Tracing to “Prove” That Leakage of Harmful Materials from a Site in Karst Terrane Will Not Occur. In: Proceedings of the Second Conference on Environmental Problems in Karst Terranes and Their Solutions (Nashville, TN), National Water Well Association, Dublin, OH, pp. 265–288.

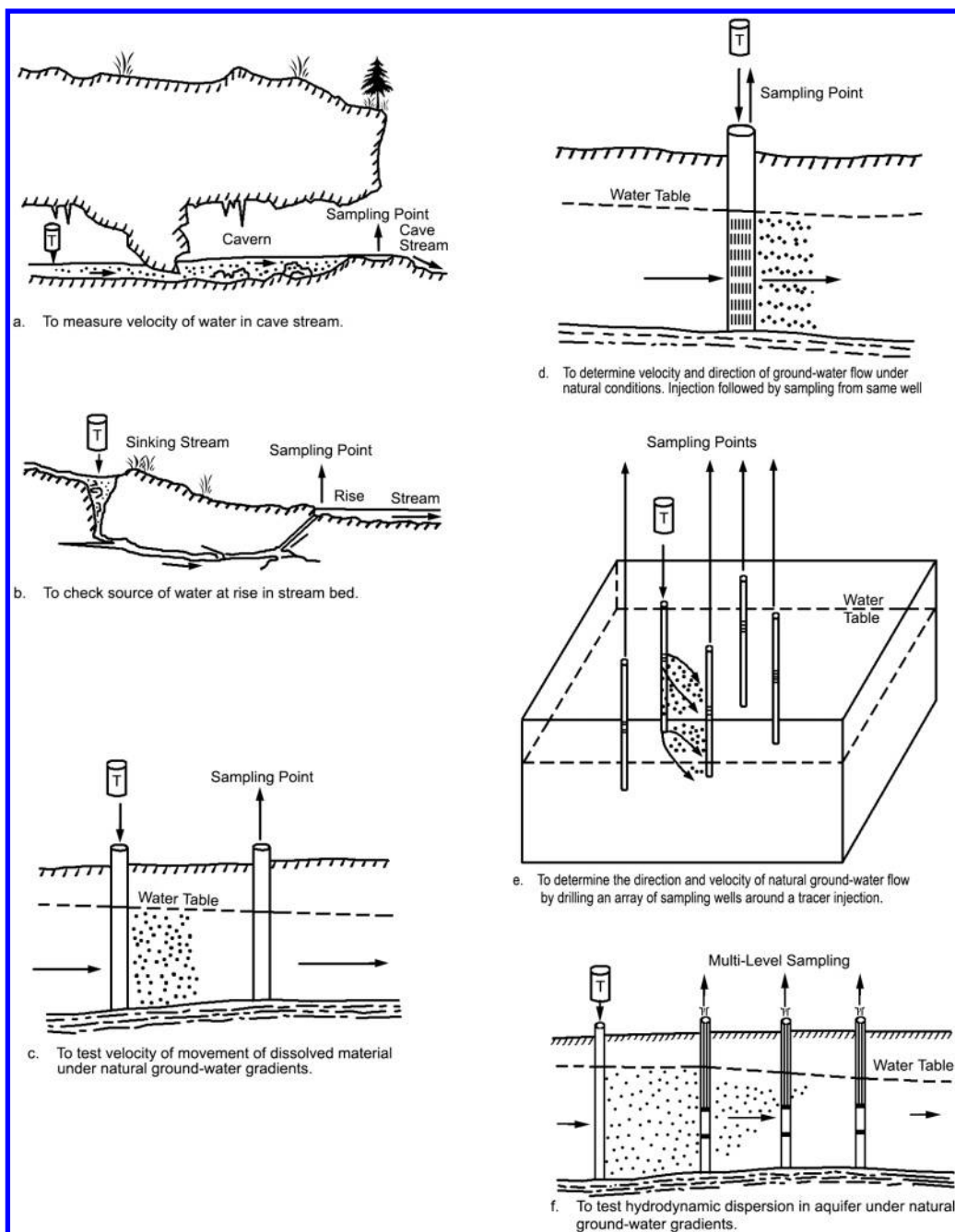


Figure 8.1 Common configurations for use of tracers to measure hydrogeologic parameters using natural gradient flow (Boulding, 1991, after Davis et al., 1985).

between two wells is shown in Figure 8.1c. Both velocity and direction of flow can be measured in a single well, as shown in Figure 8.1d (see [Section 8.5.2](#)), and by use of multiple downgradient sampling wells, as shown in Figure 8.1e. Finally, hydrodynamic dispersion can be measured by multiwell, multilevel sampling downgradient (Figure 8.1f).

Figure 8.2 shows four examples of measurement by tracers of hydrogeologic parameters using induced flow. A tracer in surface water combined with pumping from a nearby well can verify a

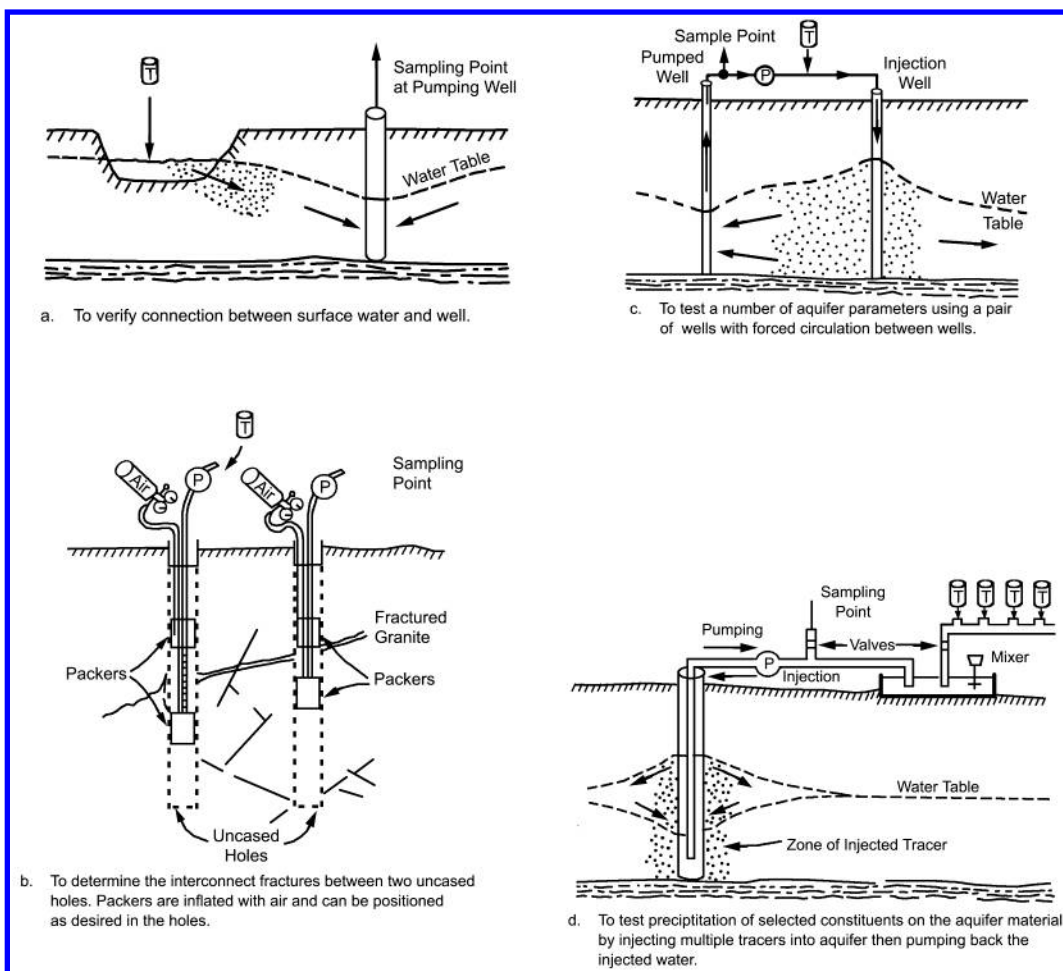


Figure 8.2 Common configurations for use of tracers to measure hydrogeologic parameters using induced flow (Boulding, 1991, after Davis et al., 1985).

connection, as shown in (Figure 8.2a). Interconnections between fractures can be mapped using tracers and inflatable packers in two uncased wells, as in Figure 8.2b. Figure 8.2c shows the measurement of a number of aquifer parameters using a pair of wells with forced circulation between wells. Figure 8.2d shows the evaluation of geochemical interactions between multiple tracers and aquifer material by alternating injection and pumping.

Other examples of the uses of tracers include determining ground-water recharge using environmental isotopes (Bradbury, 1991; Vogel et al., 1974)² and dating of ground water (Davis and Bentley, 1982/T8.5).

8.1.2 Delineation of Contaminant Sources and Plumes

Any contaminant that moves in ground water acts as a tracer; thus the contaminant itself may be mapped, or other tracers may be added to map the velocity and direction of the flow. Contaminant plumes (Section 4.7) are not tracers in the sense used in this chapter and are not discussed further here. However, Figure 8.3 shows three examples of noncontaminant tracers used to identify con-

² Bradbury, K.R. 1991. Tritium as an Indicator of Ground-Water Age in Central Wisconsin. *Ground Water* 29:398–404.
Vogel, J.C., L. Thilo, and M. Van Dijken. 1974. Determination of Groundwater Recharge with Tritium. *Journal of Hydrology* 23:131–140.

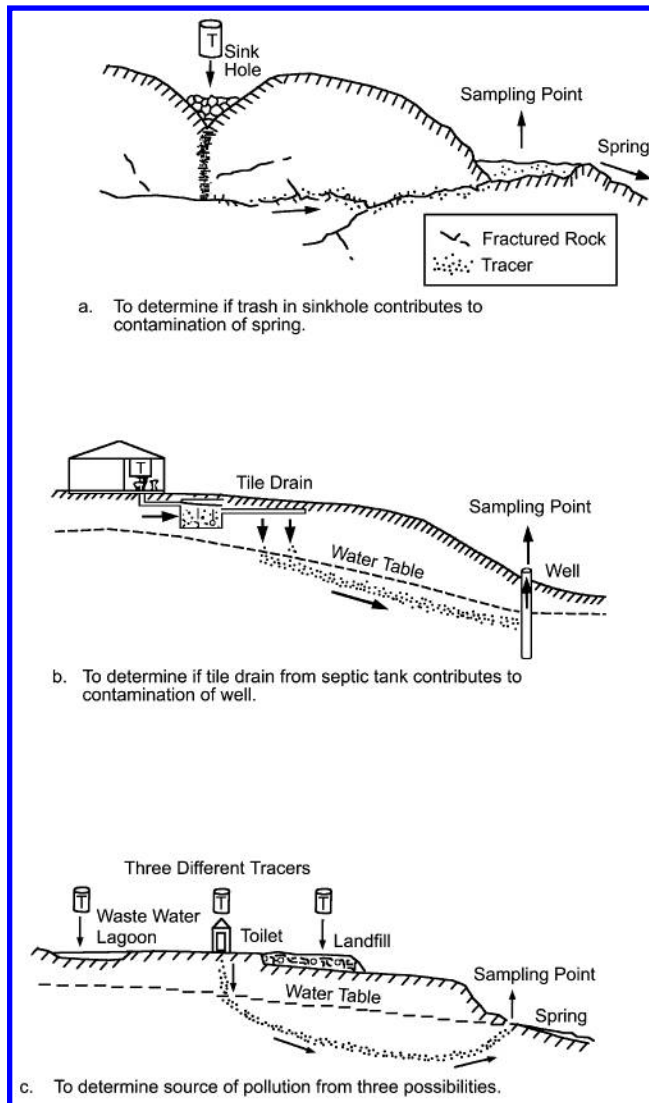


Figure 8.3 Common configurations for use of tracers to identify contaminant sources using natural gradient flow (Boulding, 1991, after Davis et al., 1985).

taminant sources and flow patterns. Figure 8.3a shows the use of a tracer in a sinkhole to determine if trash at a particular location is contributing to contamination of a spring. Similarly, Figure 8.3b shows that by flushing a dye tracer down a toilet, one can determine whether septic seepage is causing contamination of a well or surface water. Use of multiple tracers at multiple sources of potential contamination to pinpoint the actual source is shown in Figure 8.3c.

8.1.3 Characterizing Vadose Zone Hydrology

Tracers are also useful for characterizing water flow in the vadose zone. The travel time of percolating water to the saturated zone can be determined by applying water with a tracer such as potassium bromide (KBr) to the soil surface and sampling ground water at intervals until the tracer is detected (Section 8.3.1). Dyes (Section 8.3.2) provide a relatively simple method for assessing the significance of preferential flow in soil. Water with a high concentration of dye is ponded at

the surface until a known amount has completely infiltrated into the soil. The soil is then excavated in increments with photographic documentation. If flow of soil water is fairly uniform, the entire soil matrix will be colored, but if there is strong preferential flow, channels and the interfaces of soil structural units will be colored, while other parts of the soil matrix will retain their original color.

8.2 TRACER SELECTION

8.2.1 Overview of Types of Tracers

Ground-water tracers can be broadly classified as *natural* or *environmental* tracers and *injected* tracers. Table 8.1 lists 14 natural tracers and more than 40 injected tracers. The specific characteristics of the different groups shown in Table 8.1 are discussed further in [Section 8.3](#).

The potential chemical and physical behavior of the tracer in ground water is the most important selection criterion. For most purposes, a tracer should travel with the same velocity and direction as the water and not interact with solid material. This is known as a *conservative* tracer. *Nonconservative* tracers, which tend to be slowed by interactions with the solid matrix, would be used to measure distribution coefficients (Section 4.5.2) and zones of preferential flow in the vadose zone. For most

Table 8.1 List of Major Ground Water Tracers

Natural Tracers	Injected Tracers		
	Radioactive	Active	Inactive
Stable Isotopes			Ionic Substances
Deuterium (^2H)	Tritium (^3H)	Bromine-35	Chloride salts (Na, K, Li, Ca, NH_4)
Oxygen-18	Bromine-32	Indium-39	Bromide salts (K, Li)
Carbon-12	Chromium-51	Manganese-25	Iodide salts (Na)
Carbon-13	Cobalt-58	Lanthanum-57	Nonionic Substances
Nitrogen-14	Cobalt-60	Dysprosium-68	Difluorobenzoates
Nitrogen-15	Gold-198		Fluorobenzenes
Strontium-88	Iodine-131		Sulfur hexafluoride
Sulfur-32	Krypton-85 (gas)		Fluorescent Dyes
Sulfur-34	Phosphorus-32		Fluorescene
Sulfur-36	Sodium-24		Rhodamine WT
Radioactive Isotopes	Xenon-133 (gas)		Eosin (Acid Red 87)
Tritium (^3H)			Optical brighteners
Carbon-14			Tinopal 5Bm6x (FDA 22)
Silicon-32			Direct Yellow 96
Chlorine-36			Acid Yellow 7
Argon-37			Amidorhodamine 6 (Acid Red 50)
Argon-39			Gases
Krypton-81			Helium
Krypton-85			Argon
Bromine-32			Neon
Radon-222			Krypton
Gases			Xenon
Fluorocarbons			Carbon monoxide
			Nitrous oxide
			Physical Characteristics
			Water temperature
			Flood pulse
			Particulates
			<i>Lycopodium</i> spores
			Bacteria, viruses, fungi
			Sawdust

Source: Adapted from Boulding (1993b).

uses, a tracer should be nontoxic, inexpensive, and easily detected to a low concentration with widely available and simple technology. If the tracer occurs naturally in ground water, it should be present in concentrations well above background concentrations. Finally, the tracer itself should not modify the hydraulic conductivity or other properties of the medium being studied.

No one ideal tracer has been found. Because natural systems are so complex and the requirements for the tracers themselves so numerous, the selection and use of tracers is almost as much an art as a science. The following sections discuss further the factors that should be considered in selecting a tracer.

8.2.2 Hydrogeologic Considerations

The initial step in determining the physical feasibility of a tracer test is to collect as much hydrogeologic information as possible concerning the field area. The logs of the wells at the site to be tested, or logs of the wells closest to the proposed site, will give some idea of the homogeneity of the aquifer, layers present, fracture patterns, porosity, and boundaries of the flow system. Local or regional piezometric maps, or any published reports on the hydrology of the area (including results of aquifer tests), are valuable, as they may give an indication of the hydraulic gradient and hydraulic conductivity.

Major hydrogeologic factors that should be considered when selecting a tracer include:

- *Lithology.* Fine-grained materials, particularly clays, have higher sorptive capacities than coarse-grained material. This must be considered when evaluating the potential mobility of a tracer.
- *Flow Regime.* Whether flow is predominantly through porous media (alluvium, sandstone, soil), solution features (karst limestone), or fractures will influence the choice of tracer. For example, fluorescent dyes work well in karst settings, but are less effective as ground-water tracers in porous media due to sorption effects.
- *Direction of Flow.* Knowledge of the general direction of ground-water movement is essential in tracer studies using two or more wells. Section 7.2.5 discusses possible pitfalls in estimating the direction of flow using potentiometric surface maps.
- *Travel Time.* The equation for estimating travel time is discussed in Section 2.6.5. In two-well tracer tests, travel time is required to estimate spacing for wells.
- *Dispersion.* The importance of hydrodynamic dispersion in contaminant movement has been discussed in Section 4.4.2. Tracer tests are often used to measure dispersion (Figure 8.1f). In two-well tests, some preliminary estimates may be required to estimate the quantity of tracer to inject so that concentrations will be high enough to detect.

8.2.3 Tracer Characteristics

Tracers have a wide range of physical, chemical, and biological characteristics. These properties, as they relate to hydrogeologic (Section 8.2.2) and other factors (Section 8.2.4), will determine the most suitable tracer for the purposes desired.

Detectability. Injected tracers should have no, or very low, natural background levels. The lower the detection limit for instruments (parts per million, parts per billion, parts per trillion), the better. The degree of dilution is a function of type of injection, distance, dispersion, porosity, and hydraulic conductivity. Too much dilution may result in failure to observe the tracer when it reaches a sampling point because concentrations are below the detection limit. Possible interferences due to other tracers and natural water chemistry may have the same effect.

Mobility. Conservative tracers used to measure aquifer parameters such as flow direction and velocity should be (1) stable (i.e., not subject to transformation by biodegradation or nonbiological processes during the length of the test and analysis), (2) soluble in water, (3) of a similar density and viscosity (see Section 4.4.3), and (4) not subject to adsorption or precipitation. Nonconservative

nontoxic tracers used to simulate transport of contaminants should have adsorptive and other chemical properties similar to those of the contaminant of concern.

Toxicity. Nontoxic tracers should be used if at all possible. If a tracer may be toxic at certain concentrations, maximum permissible levels as determined by federal, state, or county agencies must be considered in relation to expected dilution and proximity to drinking water sources (see Section 8.2.4). Most agencies have set no limits, partly because the commonly used tracers are nontoxic in concentrations usually employed, and partly because they never considered tracers to be a problem demanding regulation.

8.2.4 Other Considerations

A tracer may have suitable characteristics for the desired purpose and the hydrogeologic setting, yet still not be suitable for reasons of economics, technological availability or sophistication, or public health.

Economics. The tracer or the instrumentation to analyze samples may be expensive. In this situation, another less expensive tracer with somewhat less favorable characteristics may suffice.

Technology. Some tracers may be difficult to obtain or may require more complicated sampling methods. Gases, for example, will escape easily from poorly sealed containers. Similarly, instrumentation for gas or isotope analyses may not be available. For example, very few laboratories are able to perform analyses of ^{36}Cl (Davis et al., 1985/T8.5). On the other hand, increasing availability of field analytical methods such as gas chromatographs (Section 9.6) means that technology is less of a limiting consideration that it was, say, 10 years ago.

Public Health. The artificial introduction of tracers must involve a careful consideration of possible health implications. Health issues involving specific tracers are identified in [Section 8.3](#). Some local or state health agencies insist on review authority prior to use of artificially introduced tracers, but most do not. Local citizens must be informed of the tracer injections, and usually the results should be made available to the public. Under some circumstances, analytical work associated with tracer studies must be performed in appropriately certified laboratories. These are job-specific decisions.

8.2.5 Tracing in Karst vs. Porous Media

Ground-water flow in karst terranes is characterized by conduit flow and diffuse flow through often complex subsurface channel systems. Ground-water contaminants tend to move rapidly in karst and resurge at the surface in locations that cannot be readily predicted from the morphology of surface drainage patterns. In contrast, ground-water flow in porous media is characterized by slow travel times and more generally predictable flow directions. These differences require substantially different approaches to conducting tracer tests as discussed in [Section 8.4](#) (karst) and [Section 8.5](#) (porous media).

8.3 TYPES OF TRACERS

Hundreds, and possibly thousands, of substances have been used as tracers in ground water, considering the full range of organic ground-water contaminants. The most commonly used tracers can be conveniently grouped into six categories: (1) ions, (2) dyes, (3) gases, (4) isotopes (including stable and radioactive isotopes), (5) water temperature, and (6) particulates. These categories are not mutually exclusive (i.e., isotopes may take the form of ions or gases). Selected tracers in each category are discussed in the following sections in relation to applicability in different hydrologic settings, field methods, and type of detection used.

8.3.1 Ions

Inorganic ionic compounds such as common salts have been used extensively as ground-water tracers. This category of tracers includes those compounds that undergo ionization in water, resulting in their separation into charged species possessing a positive charge (cations) or a negative charge (anions). The charge on an ion affects its movement through aquifers by numerous mechanisms.

Ionic tracers have been used as tools for a wide range of hydrologic problems dealing with the determination of flow paths and residence time and the measurement of aquifer properties. Slichter (1902, 1905)³ was probably the first to use ionic tracers for the study of ground water in the U.S. Specific characteristics of individual ions or ionic groups may approach those of an ideal tracer, particularly dilute concentrations of certain anions.

In most situations, anions (negatively charged ions) are not affected by the aquifer medium. Mattson (1929),⁴ however, has shown that the capacity of clay minerals for holding anions increases with decreasing pH. Under conditions of low pH, anions in the presence of clay, other minerals, or organic detritus may undergo anion exchange. Other possible effects include anion exclusion and precipitation–dissolution reactions. Cations (positively charged ions) react much more frequently with clay minerals through the process of cation exchange, which displaces other cations such as sodium and calcium into solution (Section 3.2.2). Due to their interaction with the aquifer media, little work has been done with cations. However, natural variations in Ca and Mg concentrations have been used to separate base flow and storm flow components in a karst aquifer (Dreiss, 1989).⁵

One advantage of simple ionic tracers is that they do not decompose and thus are not lost from the system. However, a large number of ions (including Cl^- and NO_3^-) have high natural background concentrations, thus requiring the injection of a tracer of high concentration. More importantly, several hundred pounds of chloride or nitrate may have an adverse effect on water quality and biota, thus becoming a pollutant. This may also result in density separation and gravity segregation during the tracer test (Grisak and Pickens, 1980).⁶ Density differences will alter flow patterns, the degree of ion exchange, and secondary chemical precipitation, all of which may change the aquifer permeability. Comparisons of tracer mobilities under laboratory and field conditions by Everts et al. (1989/T8.5) found bromide (Br^-) to be only slightly less mobile than nitrate. The generally low background concentrations of bromide often make it the ion of choice when a conservative tracer is desired.

Various applications of ionic tracers have been described in the literature. Murray et al. (1981)⁷ used lithium bromide (LiBr) in carbonate terrane to establish a hydraulic connection between a landfill and a freshwater spring, where use of Rhodamine WT dye tracer proved inappropriate. Sodium chloride (NaCl) was used by Mather et al. (1969)⁸ to investigate the influence of mining subsidence on the pattern of ground-water flow. Schmotzer et al. (1973)⁹ used postsampling neutron activation to detect a Br^- tracer. Chloride (Cl^-) and calcium (Ca^{+}) were used by Grisak and Pickens (1980 — footnote 6) to study solute transport mechanisms in fractures. Potassium (K^{+}) was used to determine leachate migration and the extent of dilution by receiving waters located by a waste

³ Slichter, C.S. 1902. The Motions of Underground Waters. U.S. Geological Survey Water Supply and Irrigation Paper 67. Slichter, C.S. 1905. Field Measurement of the Rate of Movement of Underground Waters. U.S. Geological Survey Water Supply and Irrigation Paper 140, pp. 9–34.

⁴ Mattson, W. 1929. The Laws of Soil Colloidal Behavior I. Soil Science 27/28:71–87.

⁵ Dreiss, S.J. 1989. Regional Scale Transport in a Karst Aquifer: 1. Component Separation of Spring Flow Hydrographs. Water Resources Research 25(1):117–125.

⁶ Grisak, G.E. and J.F. Pickens. 1980. Solute Transport through Fractured Media: 2. Column Study of Fractured Till. Water Resources Research 16(4):731–739.

⁷ Murray, J.P., J.V. Rouse, and A.B. Carpenter. 1981. Groundwater Contamination by Sanitary Landfill Leachate and Domestic Wastewater in Carbonate Terrain: Principle Source Diagnosis, Chemical Transport Characteristics and Design Implications. Water Research 15(6):745–757.

⁸ Mather, J.D., D.A. Gray, and D.G. Jenkins. 1969. The Use of Tracers to Investigate the Relationship between Mining Subsidence and Groundwater Occurrence of Aberdare, South Wales. Journal of Hydrology 9:136–154.

⁹ Schmotzer, J.K., W.A. Jester, and R.R. Parizek. 1973. Groundwater Tracing with Post Sampling Activation Analysis. Journal of Hydrology 20:217–236.

disposal site (Ellis, 1980).¹⁰ In vadose zone applications, Tennyson and Settergren (1980)¹¹ used bromide (Br^-) to evaluate pathways and transit time of recharge through soil at a proposed sewage effluent irrigation site, and Morrison and Lowery (1990)¹² used KBr to assess the sampling radius of a porous cup soil water sampler.

The use of *nonionic* organic compounds that are not dyes (see below) as injected tracers is a relatively recent development. Ilgenfritz et al. (1988) suggested using fluorobenzene as a field monitoring tracer that would not be likely to occur in normal industrial and commercial activities, and Bowman and Gibbons (1992) identify difluorobenzoates as good nonreactive tracers in soil and ground water.¹³ Wilson and Mackay (1993)¹⁴ found that sodium hexafluoride (SF_6), a *nonionic inorganic* compound, was as conservative a bromide as a tracer in saturated sandy media with the advantage that much lower amounts needed to be injected compared to bromide because detection limits are much lower (5 $\mu\text{g/l}$ compared to 0.5 mg/l).

8.3.2 Dyes

Dyes are relatively inexpensive, simple to use, and effective. Either fluorescent or nonfluorescent dyes may be useful in studies of water movement in soil if the soil material that has absorbed the dye is excavated and visually inspected (Section 8.1.3). Fluorescent dyes are preferable to nonfluorescent varieties in ground-water tracer studies because they are easier to detect. Dole (1906)¹⁵ was the first to recommend use of dyes for the study of ground water in the U.S. by reporting the results of use of fluorescein and other dyes in France beginning around 1882. Stiles et al. (1927)¹⁶ conducted early experiments using uranine (fluorescein) to demonstrate pollution of wells in a sandy aquifer, and Meinzer (1932)¹⁷ described use of fluorescein as a ground-water tracer. However, extensive use of fluorescent dyes for ground-water tracing did not begin until after 1960. Quinlan (1986)¹⁸ provides a concise, but comprehensive, guide to the literature on dye tracing.

The advantages of using fluorescent dyes include their very high detectability, rapid field analysis, and relatively low cost and low toxicity. Smart and Laidlaw (1977/T8.5) classified commonly used fluorescent dyes by color: orange (Rhodamine B, Rhodamine WT, and Sulforhodamine B), green (fluorescein, Lissamine FF, and pyranine), and blue — also called optical brighteners. Dyes can also be classified according to the detector (also called bug) used to recover them: dyes recovered on cotton include optical brighteners (such as Tinopal 5BM GX and Phorwhite BBH) and Direct Yellow 96, and dyes recovered on activated charcoal (fluorescein and Rhodamine WT).

The literature on use of fluorescent dyes is plagued by a lack of consistency in dye nomenclature (Quinlan, 1986 — footnote 18). The standard reference to dyes is the *Color Index* (CI) (SDC & AATC, 1971–1982).¹⁹ Most dyes are classified according to the CI Generic Name (related to method

¹⁰ Ellis, J. 1980. A Convenient Parameter for Tracing Leachate from Sanitary Landfills. *Water Research* 14(9):1283–1287.

¹¹ Tennyson, L.C. and C.D. Settergren. 1980. Percolate Water and Bromide Movement in the Root Zone of Effluent Irrigation Sites. *Water Resources Bulletin* 16(3):433–437.

¹² Morrison, R.D. and B. Lowery. 1990. Sampling Radius of a Porous Cup Sampler: Experimental Results. *Ground Water* 28(2):262–267.

¹³ Ilgenfritz, E.M., F.A. Blanchard, R.L. Masselink, and B.K. Panigrahi. 1988. Mobility and Effects in Liner Clay of Fluorobenzene Tracer and Leachate. *Ground Water* 26(1):22–30.

Bowman, R.S. and J.F. Gibbons. 1992. Difluorobenzoates as Nonreactive Tracers in Soil and Ground Water. *Ground Water* 30:8–14.

¹⁴ Wilson, R.D. and D.M. Mackay. 1993. The Use of Sulphur Hexafluoride as a Conservative Tracer in Saturated Sandy Media. *Ground Water* 31(5):719–724.

¹⁵ Dole, R.B. 1906. Use of Fluorescein in the Study of Underground Waters. U.S. Geological Survey Water Supply and Irrigation Paper 160, pp. 73–85.

¹⁶ Stiles, C.W., H.R. Crohurst, and G.E. Thomson. 1927. Uranin Test to Demonstrate Pollution of Wells. In: *Experimental Bacterial and Chemical Pollution of Wells via Ground Water and the Factors Involved*, U.S. Public Health Service Hygienic Laboratory Bulletin 147, pp. 84–87.

¹⁷ Meinzer, O.E. 1932. Outline of Methods for Estimating Ground Water Supplies. U.S. Geological Survey Water Supply Paper 638-C, pp. 126–131.

¹⁸ Quinlan, J.F. 1986. Discussion of “Ground Water Tracers” by Davis et al. (1985) with Emphasis on Dye Tracing, Especially in Karst Terranes. *Ground Water* 24(2):253–259 and 24(3):396–397. [References]

¹⁹ SDC & AATC (Society of Dyers & Colorists and American Association of Textile Chemists). 1971–1982. *Color Index*, 3rd ed.

of dyeing) and chemical structure (the CI Constitution Number). Abrahart (1968, pp. 15–43)²⁰ provides a concise guide to dye nomenclature. Dyes are also classified according to their use in foods, drugs, and cosmetics (Marmion, 1984).²¹ There are numerous commercial names for most dyes. Consequently, reported results of dye-tracing experiments should always specify (1) the CI Generic Name or CI Constitution Number, and (2) the manufacturer and the manufacturer's commercial name. The full name of the dye should be mentioned at least once to distinguish it from other dyes with the same or similar names. For example, in 1985, four structurally different kinds of Rhodamine were sold in the U.S. under 11 different names by five manufacturers, and there are more than 180 kinds of Direct Yellow dye (Quinlan, 1986 — footnote 18).

The first part of the commercial name of a dye should not be confused with the dye itself. For example, Tinopal and Phorwhite are trade names used for whole series of chemically unrelated dyes made by a single company and should be capitalized. Seven chemically different Tinopals and 20 different Phorwhites are currently sold in the U.S. as optical brighteners.

A particularly confusing point of dye nomenclature is that there are two fluorescein dyes with the same CI Name and Number, although they do have different D&C (drug and cosmetic) designations: fluorescein ($C_{20}H_{12}O_5$), D&C Yellow 7; and fluorescein sodium ($C_{20}H_{12}O_5Na_2$), D&C Yellow 8. Only D&C Yellow 8 is soluble in water and hence suitable for ground-water tracing. In the American and British literature this is referred to as *fluorescein*, whereas in the European literature it is called *uranine*.

Although fluorescent dyes exhibit many of the properties of an ideal tracer, a number of factors interfere with concentration measurement. Fluorescence is used to measure dye concentration, but the amount of fluorescence may vary with suspended sediment load, temperature, pH, $CaCO_3$ content, salinity, etc. Other variables that affect tracer test results are quenching (some emitted fluorescent light is reabsorbed by other molecules), adsorption, and photochemical and biological decay. A disadvantage of fluorescent dyes in tropical climates is poor performance resulting from chemical reactions with dissolved carbon dioxide (Smart and Smith, 1976).²²

Fluorescence intensity is inversely proportional to temperature. Smart and Laidlaw (1977/T8.5) described the numerical relationship and provided temperature correction curves. Low pH tends to reduce fluorescence. Figure 8.4 shows that the fluorescence of Rhodamine WT decreases rapidly at increasingly acidic pH values below about 6.0. An increase in the suspended sediment concentration also generally causes a decrease in fluorescence.

Dyes travel slower than water due to sorption and are generally not as conservative as radioactive tracers or some of the ionic tracers. Sorption can occur on organic matter, clays (bentonite, kaolinite, etc.), sandstone, limestone, plants, plankton, and even glass sample bottles. Typically, fluorescence decreases with an increase in suspended sediment concentration, and this interference makes it hard to interpret tracer measurements for water flow.

These sorption effects are a strong incentive to choose a dye that is nonsorptive for the type of medium tested. Different dyes vary greatly in amount of sorption on specific materials. For example, Repogle et al. (1966)²³ measured sorption of three orange dyes on bentonite clay with the following results: Rhodamine WT, 28%; Rhodamine B, 65%; and Sulforhodamine B, 96%.

Smart (1984/T8.5), in a review of the toxicity of 12 fluorescent dyes, identified only three tracers (Tinopal CBS-X, fluorescein, and Rhodamine WT) with no demonstrated carcinogenic or mutagenic hazard. He recommended against the use of Rhodamine B because it is a known carcinogen. Use of the other dyes was considered acceptable provided normal precautions are observed during dye handling. Aulenbach et al. (1978/T8.5) concluded that Rhodamine B should not be used as a ground-water tracer simply on the basis of sorption losses.

²⁰ Abrahart, E.N. 1968. Dyes and Their Intermediates. Pergamon Press, Oxford.

²¹ Marmion, D.M. 1984. Handbook of U.S. Colorants for Foods, Drugs, and Cosmetics, 2nd ed. Wiley Interscience, New York.

²² Smart, P.L. and D.I. Smith. 1976. Water Tracing in Tropical Regions: The Use of Fluorometric Techniques in Jamaica. Journal of Hydrology 30:179–195.

²³ Repogle, J.A., L.E. Myers, and K.J. Brust. 1966. Flow Measurements with Fluorescent Tracers. Journal of Hydraulics Division ASCE 92:1–15.

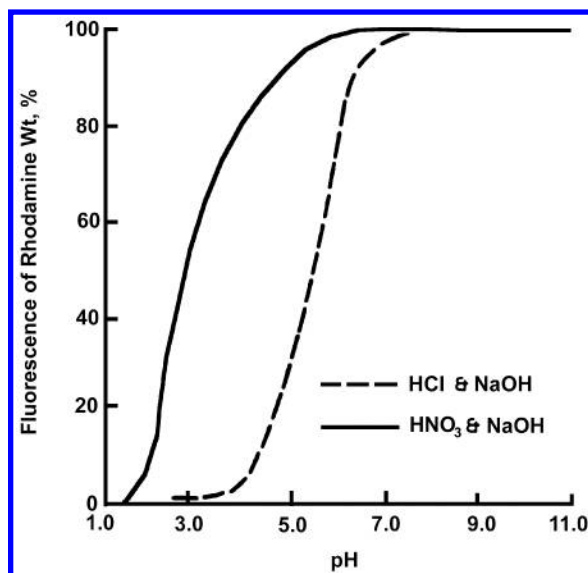


Figure 8.4 The effect of pH on Rhodamine WT (Davis et al., 1985, after Smart and Laidlaw, 1977).

Currently, the U.S. Geological Survey has a policy of limiting the maximum concentration of fluorescent dyes at water-user withdrawal points to 0.01 ppm (Hubbard et al., 1982/T8.5). This is a conservative, nonobligatory limit, and Field et al. (1990/T8.5) recommend that tracer concentrations not exceed 1 ppm for a period in excess of 24 h in ground water, and careful evaluation of a tracer before use in a sensitive or unique ecosystem. Dyes should probably not be used where water supplies are chlorinated because dye molecules may react with chlorine to form chlorophenols (Smart and Laidlaw, 1977/T8.5).

Fluorescein, also known as uranine, sodium fluorescein, and by other names, has been one of the most widely used green dyes. Like all green dyes, its use is commonly complicated by high natural background fluorescence, which lowers sensitivity of analyses and makes interpretation of results more difficult. However, fluorescein is the most common dye used for tracing ground water in karst.

Lewis et al. (1966)²⁴ used fluorescein in a fractured rock study. Mather et al. (1969 — footnote 8) recorded its use in a mining subsidence investigation in South Wales. Tester et al. (1982)²⁵ used fluorescein to determine fracture volumes and diagnose flow behavior in a fractured granitic geothermal reservoir. They found no measurable adsorption or decomposition of the dye during the 24-h exposures to rocks at 392°F. At the other extreme, Rahe et al. (1978/T8.5) did not recover any injected dye in their hill slope studies, even at a distance of 2.5 m downslope from the injection point. The same experiment used bacterial tracers successfully. Sabatini and Austin (1991)²⁶ used the sorption characteristics of fluorescein (less sorptive) and Rhodamine WT (more sorptive) to delimit the expected appearance times of the pesticides atrazine and arachlor (intermediate sorption characteristics) in a sandy alluvial aquifer.

Another green fluorescent dye, *pyranine*, has a stronger fluorescent signal than does fluorescein, but is much more expensive. It has been used in several soil studies. Reynolds (1966)²⁷ found pyranine

²⁴ Lewis, D.C., G.J. Kriz, and R.H. Burg. 1966. Tracer Dilution Sampling Technique to Determine Hydraulic Conductivity of Fractured Rock. *Water Resources Research* 2:533–542.

²⁵ Tester, J.W., R.L. Bivens, and R.M. Potter. 1982. Interwell Tracer Analysis of a Hydraulically Fractured Granitic Geothermal Reservoir. *Society of Petroleum Engineers Journal* 8:537–554.

²⁶ Sabatini, D.A. and T.A. Austin. 1991. Characteristics of Rhodamine WT and Fluorescein as Adsorbing Ground-Water Tracers. *Ground Water* 29(3):341–349.

²⁷ Reynolds, E.R.C. 1966. The Percolation of Rainwater through Soil Demonstrated by Fluorescent Dyes. *Journal of Soil Science* 17(1):127–132.

to be the most stable dye used in an acidic, sandy soil. Drew and Smith (1969/T8.5) stated that pyranine is not as easily detectable as fluorescein, but is more resistant to decoloration and adsorption. Pyranine has a very high photochemical decay rate and is strongly affected by pH in the range found in most natural waters (McLaughlin, 1982/T8.5).

Rhodamine WT has been considered one of the most useful tracers for quantitative studies, based on minimum detectability, photochemical and biological decay rates, and adsorption (Knuttsen, 1968/T8.5; Smart and Laidlaw, 1977/T8.5; Wilson et al., 1986/T8.5). Rhodamine WT is the most conservative dye available for stream tracing (Hubbard et al., 1982/T8.5) and is also commonly used in karst tracing studies. It is not a suitable tracer, however, for low pH environments (Figure 8.4).

Gann and Harvey (1975)²⁸ used Rhodamine WT for karst tracing in a limestone and dolomite system in Missouri. Aulenbach et al. (1978/T8.5) compared Rhodamine B, Rhodamine WT, and tritium as tracers in effluent from a sewage treatment plant that was applied to natural delta sand beds. The Rhodamine B was highly adsorbed, while the Rhodamine WT and tritium yielded similar breakthrough curves. Aulenbach and Clesceri (1980)²⁹ also used Rhodamine WT successfully in a sandy medium. Shiau et al. (1993)³⁰ found that the two-step breakthrough curve that is often observed when Rhodamine WT is used in porous media is the result of two isomers each having different sorptive characteristics. This effect may lead to an incorrect interpretation of a bicontinuum flow system.

Rhodamine B and Sulforhodamine B are poor tracers for use in ground water and most surface waters. It could be said the B stands for bad. Amidorhodamine G is a significantly better tracer; similarly, it can be said that the G stands for good.³¹

Blue fluorescent dyes, or *optical brighteners*, have been used in increasing amounts in the past decade in textiles, paper, and other materials to enhance their white appearance. Water that has been contaminated by domestic waste entering septic tank soil absorption fields can be used as a “natural” tracer if it contains detectable amounts of the brighteners. Glover (1972)³² was the first to describe the use of optical brighteners in karst environments. Since then, they have been extensively used in the U.S. The tracer *Amino G acid* is a dye intermediate used in the manufacture of dyes that is sometimes mistakenly classified as an optical brightener (Quinlan, 1986 — footnote 18). Amino G acid is now recognized as carcinogenic and should not be used in water that might be used for drinking (see footnote 31). Smart and Laidlaw (1977/T8.5) provide detailed information on the characteristics of the optical brightener Photine CU and Amino G acid.

8.3.3 Gases

Numerous natural and artificially produced gases have been found in ground water. Some of the naturally produced gases can serve as tracers, and gas can also be injected into ground water where it dissolves and serves as a tracer. Only a few examples of gases being used as ground-water tracers are found in the literature, however. Table 8.2 lists gases of potential use in hydrogeologic studies. Gases are useful tracers in the saturated zone. They are less reliable in the unsaturated zone because bleeding into the atmosphere can give false negative results.

Inert Natural Gases. Because of their nonreactive and nontoxic nature, noble gases are potentially useful tracers. Helium is used widely as a tracer in industrial processes. Carter et al. (1959)³³

²⁸ Gann, E.E. and E.J. Harvey. 1975. Norman Creek: A Source of Recharge to Maramec Spring, Phelps County, Missouri. Journal of Research of the U.S. Geological Survey 3(1):99–102.

²⁹ Aulenbach, D.B. and N.L. Clesceri. 1980. Monitoring for Land Application of Wastewater. Water, Air, and Soil Pollution 14:81–94.

³⁰ Shiau, B.-J., D.A. Sabatini, and J.H. Harwell. 1993. Influence of Rhodamine WT Properties on Sorption and Transport in Subsurface Media. Ground Water 31(6):913–920.

³¹ Personal communication, James Quinlan, Nashville, TN, July 1990.

³² Glover, R.R. 1972. Optical Brighteners: A New Water Tracing Reagent. Transactions of the Cave Research Group (Great Britain) 14(2):84–88.

³³ Carter, R.C., W.J. Kaufman, G.T. Orlob, and D.K. Todd. 1959. Helium as a Ground-Water Tracer. Journal of Geophysical Research 64:2433–2439.

Table 8.2 Gases of Potential Use as Tracers

	Approximate Natural Background Assuming Equilibrium with Atmosphere at 20°C (mg gas/l water)	Maximum Amount in Solution Assuming 100% Gas at Pressure of 1 atm at 20°C (mg gas/l water)
Argon	0.57	60.6
Neon	1.7×10^{-4}	9.5
Helium	8.2×10^{-6}	1.5
Krypton	2.7×10^{-4}	234
Xenon	5.7×10^{-5}	658
Carbon monoxide	6.0×10^{-6}	28
Nitrous oxide	3.3×10^{-4}	1100.0

Source: Boulding (1991), after Davis et al. (1985).

studied the feasibility of using helium as a tracer in ground water and found that it traveled at a slightly lower velocity than chloride. Advantages of using helium as a tracer are its (1) safety, (2) low cost, (3) relative ease of analysis, (4) low concentrations required, and (5) chemical inertness. Disadvantages identified in this study included (1) relatively large errors in analysis, (2) difficulties in maintaining a constant recharge rate, (3) time required to develop equilibrium in unconfined aquifers, and (4) possible loss to the atmosphere in unconfined aquifers. Relatively recent improvements of field instrumentation for detection of helium as described in tracing experiments conducted in a basalt aquifer in Hawaii now make use of helium a practical and convenient method (Gupta et al., 1994).³⁴

Neon, krypton, and xenon are other possible candidates for injected tracers because their natural concentrations are very low (Table 8.2). Although the gases do not undergo chemical reactions and do not participate in ion exchange, the heavier noble gases (krypton and xenon) do sorb to some extent on clay and organic material. The solubility of the noble gases decreases with increases in temperature. Therefore, the natural concentrations of these gases in ground water are an indication of surface temperatures at the time of water infiltration. This property has been used to reconstruct palaeoclimatic trends in a sandstone aquifer in England using argon and krypton for age estimates (Andrews and Lee, 1979).³⁵ Sugisaki (1969)³⁶ and Mazor (1972)³⁷ have also used natural inert gases in this way.

Anthropogenic Gases. Numerous artificial gases, such as fluorocarbons, have been manufactured during the past decade, and several of them have been released in sufficient volumes to produce measurable concentrations in the atmosphere on a worldwide scale. One of the most interesting groups of these gases is the fluorocarbons. These gases generally pose a very low biological hazard, are generally stable for periods measured in years, do not react chemically with other materials, can be detected in very low concentrations, and sorb only slightly on most minerals. However, they do sorb strongly on organic matter.

Fluorocarbons have two possible applications. First, because large amounts of fluorocarbons were not released into the atmosphere until the late 1940s and early 1950s, the presence of fluorocarbons in ground water indicates that the water was in contact with the atmosphere within the past 30 to 40 years (Thompson and Hayes, 1978).³⁸ The second possible application of fluoro-

³⁴ Gupta, S.K., L.S. Lau, and P.S. Moravcik. 1994. Ground-Water Tracing with Injected Helium. *Ground Water* 32(1):96–102.

³⁵ Andrews, J.H. and D.J. Lee. 1979. Inert Gases in Groundwater from the Bunter Sandstone of England as Indicators of Age and Palaeoclimatic Trends. *Journal of Hydrology* 41:233–252.

³⁶ Sugisaki, R. 1969. Measurement of Effective Flow Velocity of Groundwater by Means of Dissolved Gases. *American Journal of Science* 259:144–153.

³⁷ Mazor, E. 1972. Paleotemperatures and Other Hydrological Parameters Deduced from Noble Gases Dissolved in Ground Waters, Jordan Rift Valley, Israel. *Geochimica et Cosmochimica Acta* 36:1321–1336.

³⁸ Thompson, G.M. and J.M. Hayes. 1979. Trichlorofluoromethane in Ground Water, a Possible Tracer and Indicator of Ground-Water Age. *Water Resources Research* 15(3):546–554.

carbon compounds is as injected tracers (Thompson et al., 1974).³⁹ Because detection limits are so low, large volumes of water can be labeled with the tracers at a rather modest cost. The problem of sorption on natural material, especially organic matter, and concerns with effect of CFCs on the ozone layer have prevented more widespread use of fluorocarbons as tracers.

8.3.4 Isotopes

An isotope is any of two or more forms of the same element having the same atomic number and nearly the same chemical properties, but with different atomic weights and different numbers of neutrons in the nuclei. Isotopes may be *stable* (do not emit radiation) or *radioactive* (emit alpha, beta, or gamma rays). There are over 280 isotopic forms of stable elements and 40 or so radioactive isotopes. A wide variety of stable and radioactive isotopes have been used in ground-water tracer studies. There is an extensive literature on the use of isotopes in ground-water investigations (see Table 8.6). Lack of familiarity with techniques for analyzing environmental isotopes has limited their use by practicing field hydrogeologists in ground-water contamination studies. Hendry (1988)⁴⁰ recommends the use of hydrogen and oxygen isotopes as a relatively inexpensive way to estimate the age of near-surface ground-water samples.

Stable Isotopes. Stable isotopes are rarely used for artificially injected tracer studies in the field because of (1) the difficulty in detecting small artificial variations of most isotopes against the natural background, (2) the high cost of their analysis, and (3) the expense of preparing isotopically enriched tracers. The average stable isotope composition of deuterium (^2H) and ^{18}O in precipitation changes with elevation, latitude, distance from the coast, and temperature. Consequently, measurement of these isotopes in ground water can be used to trace the large-scale movement of ground water and to locate areas of recharge (Gat, 1971).⁴¹

The two abundant isotopes of nitrogen (^{14}N and ^{15}N) can vary significantly in nature. Ammonia (NH_4) escaping as vapor from decomposing animal wastes, for example, will tend to remove the lighter (^{14}N) nitrogen and will leave behind a residue rich in heavy nitrogen. In contrast, many fertilizers with an ammonia base will be isotopically light. Natural soil nitrate will be somewhat between these two extremes. As a consequence, nitrogen isotopes have been useful in determining the origin of unusually high amounts of nitrate in ground water. Also, the presence of more than about 5 mg/l of nitrate commonly is an indirect indication of contamination from chemical fertilizers and sewage. Aravena et al. (1993)⁴² used the stable isotopes ^{18}O and ^{15}N to differentiate a contaminant nitrate plume emanating from a single domestic septic system in an aquifer characterized by high and similar nitrate content both outside and inside the plume. Komor and Anderson (1993)⁴³ used ^{15}N in nitrate as a qualitative indicator of nitrate sources in ground water (animal feedlot, inorganic nitrogen fertilizer, and septic systems).

The stable sulfur isotopes (^{32}S , ^{34}S , and ^{36}S) have been used to distinguish between sulfate originating from natural dissolution of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and sulfate originating from an industrial spill of sulfuric acid (H_2SO_4).

Two stable isotopes of carbon (^{12}C and ^{13}C) and one radioisotope (^{14}C) are used in hydrogeologic studies. Although not as commonly studied as ^{14}C , the ratio of the stable isotopes, $^{13}\text{C}/^{12}\text{C}$, is potentially useful in sorting out the origins of certain contaminants found in water. For example, methane (CH_4) originating from some deep geologic deposits is isotopically heavier than methane

³⁹ Thompson, G.M., J.M. Hayes, and S.N. Davis. 1974. Fluorocarbon Tracers in Hydrology. *Geophysical Research Letters* 1:177–180.

⁴⁰ Hendry, M.J. 1988. Do Isotopes Have a Place in Ground-Water Studies? *Ground Water* 26(4):410–415.

⁴¹ Gat, J.R. 1971. Comments on the Stable Isotope Method in Regional Ground Water Investigations. *Water Resources Research* 7:980–993.

⁴² Aravena, R., M.L. Evans, and J.A. Cherry. 1993. Stable Isotopes of Oxygen and Nitrogen in Source Identification of Nitrate from Septic Systems. *Ground Water* 31(2):180–186.

⁴³ Komor, S.C. and H.W. Anderson, Jr. 1993. Nitrogen Isotopes as Indicators of Nitrate Sources in Minnesota Sand-Plain Aquifers. *Ground Water* 31(2):260–270.

Table 8.3 Commonly Used Radioactive Tracers for Ground Water Studies

Radionuclide	Half-Life	Chemical Compound
³ H	12.3 y	H ₂ O
³² P	14.3 d	Ha ₂ HPO ₄
⁵¹ Cr	27.8 d	EDTA-Cr and CrC1 ₃
⁶⁰ Co	5.25 y	EDTA-Co and K ₃ Co (CN ₆)
³² Br	33.4 h	NH ₄ Br, NaBr, LiBr
⁸⁵ Kr	10.7 y	Kr (gas)
¹³¹ I	8.1 d	I and KI
¹⁹⁸ Au	2.7 d	AuCl ₃

Note: y = year; d = day; h = hour.

Source: Boulding (1991), after Davis et al. (1985).

originating from near-surface sources. This contrast forms the basis for identifying aquifers contaminated with methane from pipelines and from subsurface storage tanks.

Isotopes of other elements such as chlorine, strontium, and boron are used more for determining regional directions of ground-water flow than for identifying sources of contamination.

Radionuclides. Radioactive isotopes of various elements are collectively referred to as radionuclides. In the early 1950s there was great enthusiasm for using radionuclides both as natural “environmental” tracers and as injected artificial tracers. However, the use of artificially injected radionuclides has all but ceased in many countries, including the U.S., because of concerns about possible adverse health effects (Davis et al., 1985/T8.5). Most uses of artificially introduced radioactive tracers are confined to carefully controlled laboratory experiments or to deep petroleum production zones that are devoid of potable water. Table 8.3 lists eight radionuclides commonly used as *injected* tracers, their half-lives, and the chemical form in which they are typically used.

The use of natural environmental tracers has expanded to the point that they are now a major component of many hydrochemical studies. A number of radionuclides are present in the atmosphere from natural and artificial sources, and many of these are carried into the subsurface by rainwater (see natural radioisotopes listed in Table 8.1). The most common hydrogeologic use of these radionuclides is in estimating the average length of time ground water has been isolated from the atmosphere. This measurement is complicated by dispersion in the aquifer and mixing in wells that sample several hydrologic zones. Nevertheless, the age of water in an aquifer can usually be established as being older than some given limiting value. For example, detection of atmospheric radionuclides might indicate that ground water was recharged more than 1000 years ago or that, in another region, all the ground water in a given shallow aquifer is younger than 30 years.

Since the 1950s, atmospheric tritium, the radioactive isotope of hydrogen (³H) with a half-life of 12.3 years, has been dominated by tritium from the detonation of thermonuclear devices. Thermonuclear explosions had increased the concentration of tritium in local rainfall to more than 1000 tritium units (TU) in the Northern Hemisphere by the early 1960s. As a result, ground water in the Northern Hemisphere with more than about 5 TU is generally less than 30 years old. Very small amounts of tritium, 0.05 to 0.5 TU, can be produced by natural subsurface processes, so the presence of these low levels does not necessarily indicate a recent age.

Nuclear bomb testing also released significant amounts of the radioactive isotope of chlorine ³⁶Cl into the atmosphere (which also contains low concentrations of cosmogenic ³⁶Cl), and this isotope occurs as a contaminant in low-level nuclear waste from nuclear fuel reprocessing. Beasley et al. (1993)⁴⁴ found this isotope to be the best indicator for delineation of contaminant plumes resulting from nuclear fuel reprocessing facilities.

The radioactive isotope of carbon, ¹⁴C (with a half-life of 5730 years), is also widely studied in ground water. In practice, the use of ¹⁴C is rarely simple. Sources of old carbon, primarily from

⁴⁴ Beasley, T.M. et al. 1993. Chlorine-36 in the Snake River Plain Aquifer at the Idaho National Engineering Laboratory: Origin and Implications. *Ground Water* 31(2):302–310.

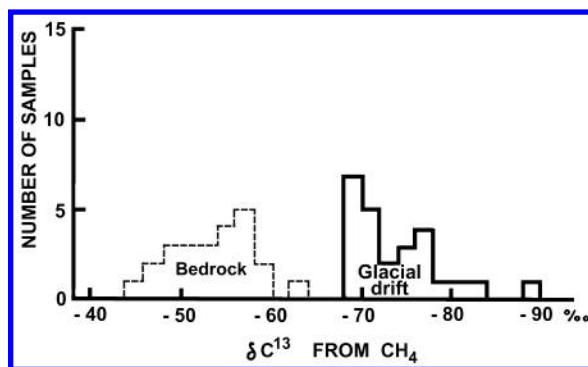


Figure 8.5 Differentiation of methane leak (bedrock) from natural shallow methane source (Davis et al., 1985, after Coleman et al., 1977).

limestone and dolomite, will dilute the sample, and a number of processes, such as the formation of CH₄ gas or the precipitation of carbonate minerals, will fractionate the isotopes and alter the apparent age. Interpreting ¹⁴C ages of water is so complex that it should be attempted only by hydrochemists specializing in isotope hydrology. Despite the complicated nature of ¹⁴C studies, they are highly useful in determining the approximate residence time of old water (500 to 30,000 years) in aquifers. In certain circumstances, this information cannot be obtained in any other way. Figure 8.5 illustrates how carbon isotope percentages allow differentiation of bedrock-derived methane leaking from a pipeline or tank from natural methane generated in shallow aquifers of glacial drift.

Inert Radioactive Gases. Chemically inert but radioactive ¹³³Xe and ⁸⁵Kr appear to be suitable for many injected tracer applications (Robertson, 1969; Wagner, 1977).⁴⁵ provided legal restrictions can be overcome. ²²²Rn, one of the daughter products from the spontaneous fission of ²³⁸U, is the most abundant of the natural inert radioactive gases. Radon is present in the subsurface, but owing to the short half-life (3.8 days) of ²²²Rn, and the absence of parent uranium nuclides in the atmosphere, radon is virtually absent in surface water that has reached equilibrium with the atmosphere. Surveys of radon in surface streams and lakes have therefore been useful in detecting locations where ground water enters surface waters (Rogers, 1958).⁴⁶ Hoehn and von Gunten (1989)⁴⁷ measured dilution of radon on ground water to assess infiltration from surface waters to the aquifer.

8.3.5 Alcohol Tracers

Aliphatic alcohols can be applied as tracers in the subsurface to determine the volume and extent of contamination in the saturated zone. Generally, these alcohols are dissolved in water at dilute concentrations and subsequently injected in the subsurface. The elution profiles of these alcohols can be evaluated at downgradient extraction wells to assess the magnitude of contamination in an aquifer. The partitioning interwell tracer test is a tracer method applied to porous media that provides a greater sampling volume for assessing contamination over conventional core sampling, cone penetrometer testing, and geophysical logging. Examples of alcohols used for partitioning tracer tests are shown in Table 8.4.

⁴⁵ Robertson, J.B. 1969. Behavior of Xenon-133 Gas after Injection Underground. U.S. Geological Survey Open File Report ID022051.

Wagner, O.R. 1977. The Use of Tracers in Diagnosing Interwell Reservoir Heterogeneities. *Journal of Petroleum Technology* 11:1410–1416.

⁴⁶ Rogers, A.S. 1958. Physical Behavior and Geologic Control of Radon in Mountain Streams. U.S. Geological Survey Bulletin 1052E:187–211.

⁴⁷ Hoehn, E. and H.J.R. von Gunten. 1989. Radon in Groundwater: A Tool to Assess Infiltration from Surface Waters to Aquifers. *Water Resources Research* 25(8):1795–1803.

Table 8.4 Alcohol Tracers Used for Partitioning Tracer Tests

Alcohol	Partition Coefficient	Contaminant Characterized
1-Propanol	0.1	DNAPL*
1-Pentanol	3.9	
2-Ethyl-1-butanol	12.5	
1-Hexanol	30.2	
1-Heptanol	140.5	LNAPL**
Ethanol	0.1	
n-Pentanol	1.4	
n-Hexanol	4.6	
2,2-Dimethyl-3-pentanol	12.9	

Source: *, Londergan et al. (2001/T8.6); **, Annable et al. (1998/T8.6).

Specifically, alcohols can be used to quantify the amount of residual dense nonaqueous phase liquids (DNAPLs) or light nonaqueous phase liquids (LNAPLs) in the subsurface. Jin et al. (1995/T8.6) have reported a method for analyzing the production well tracer response over time to determine the amount of residual NAPL in the subsurface. The theory of partitioning tracers is based on injecting a suite of alcohol tracers in the subsurface, each with different partition coefficients. The partition coefficient is the ratio of the concentration of the alcohol in the NAPL (oil) phase relative to that in the water phase at equilibrium. Dwarakanath and Pope (1998/T8.6) present a method for estimating partition coefficients based on equivalent alkane number. More rigorously, the partition coefficients of each alcohol can be measured in the laboratory between specific NAPLs of interest and the corresponding aqueous phase the NAPL is in contact with. In this fashion, the NAPL–water partition coefficients can be quantitatively determined prior to injection.

When alcohol tracers with different partition coefficients are injected into the subsurface, those with higher partition coefficients tend to selectively partition into the NAPL (oil) phase to a greater extent than tracers with lower partition coefficients. Thus, under advective flow, the nonpartitioning tracers are transported in the water phase while the partitioning tracers are transported in the NAPL phase. When the NAPL phase is at residual saturation, the tracer molecules are advected only in the water phase. The elution curves of each tracer are analyzed and compared to one another. The chromatographic separation between the partitioning and nonpartitioning tracers is proportional to the amount of NAPL saturation in the subsurface within the tracer flow field (Annable et al., 1998/T8.6; Jin et al., 1995). See [Table 8.6](#) for additional references relating to the theory and interpretation of partitioning tracers.

Example breakthrough curves of partitioning tracers used for a remedial performance assessment are shown in [Figure 8.11](#). Alcohol tracers were used to determine the volume and distribution of residual DNAPL prior to the use of surfactants for DNAPL removal from a former chemical disposal pit at Hill Air Force Base, UT. From the breakthrough curve in [Figure 8.11a](#), it can be seen that 1-propanol is the most conservative tracer while 1-heptanol is the least conservative. Londergan et al. (2001/T8.6) reported the average DNAPL saturation to be 2.7% (346 gal) over a swept pore volume of 12,940 gal. Partitioning tracers were used here to estimate the volume of contamination in the subsurface prior to remediation.

Example breakthrough curves for partitioning tracers applied after remediation are shown in [Figure 8.11b](#). The tracer curves correspond closely with one another, indicating little or no DNAPL to retard the partitioning tracers prior to their arrival at the extraction wells. Using the method of moments reported by Jin et al. (1995/T8.6) to evaluate the tracer response curves, Londergan et al. (2001/T8.6) reported the final, posttreatment DNAPL saturation to be 0.035% (5 gal) remaining in the swept pore volume of 15,360 gal. Alcohol tracers were used as the primary performance assessment for the remedial action at this site, indicating approximately 98% removal efficiency. Many other remedial actions have utilized the partitioning tracer tests as a measure of performance for the applied remedial technology. References where alcohols have been used as partitioning tracers for LNAPL and DNAPL site characterization are listed in [Table 8.6](#).

8.3.6 Water Temperature

The temperature of water changes slowly as it migrates through the subsurface, because water has a high specific heat capacity compared to most natural materials. For example, temperature anomalies associated with the spreading of warm wastewater in the Hanford Reservation in south-central Washington have been detected more than 8 km (5 mi) from the source.

Water temperature is a potentially useful tracer, although it has not been used frequently. The method should be applicable in granular media, fractured rock, or karst regions. Keys and Brown (1978)⁴⁸ traced thermal pulses resulting from the artificial recharge of playa lake water into the Ogallala formation in Texas. They described the use of temperature logs (temperature measurements at intervals in cased holes) to detect hydraulic conductivity differences in an aquifer. Temperature logs are a relatively simple and useful borehole logging method (Table 6.6).

Changes in water temperature are accompanied by changes in water density and viscosity, which in turn alter the velocity and direction of flow. For example, injected ground water with a temperature of 40°C will travel more than twice as fast in the same aquifer under the same hydraulic gradient as water at 5°C. Because the warm water has a slightly lower density than cold water, buoyant forces give rise to flow that “floats” on top of the cold water. To minimize problems of temperature-induced convection, very accurately measured small temperature differences should be used if hot or cold water is in the introduced tracer.

Figure 8.6 illustrates use of temperature as a tracer for small-scale field tests, using shallow drive-point wells 2 ft apart in an alluvial aquifer. The transit time of the peak temperature was about 107 min, while the resistivity data indicated a travel time of about 120 min. The injected water had a temperature of 38°C, while the ground-water temperature was 20°C; the peak temperature obtained in the observation well was 27°C.

In these tests, temperature indicated breakthrough of the chemical tracers, aiding in the timing of sampling. It was also useful as a simple, inexpensive tracer for determining the correct placement of sampling wells.

Another application of water-temperature tracing is the detection of river recharge in an aquifer. Most rivers have large seasonal water temperature fluctuations. If the river is recharging an aquifer, the seasonal fluctuations can be detected in the ground water adjacent to the river (Rorabaugh, 1956).⁴⁹

8.3.7 Particulates

Solid material in suspension, such as spores, can be a useful tracer in areas where water flows in large conduits such as in some basalt, limestone, or dolomite aquifers. Seismic methods at the surface have been used to detect the location of time-delayed explosives floating through a cave system (Arandjelovic, 1969).⁵⁰ Small particulate tracers, such as bacteria, can travel through any porous media such as soils and fractured bedrock where the pore size is larger than the size of the microorganism. Microorganisms are probably the most commonly used particulate tracers. Table 8.5 compares characteristics of microbial tracers.

Yeast. The use of baker’s yeast (*Saccharomyces cerevisiae*) as a ground-water tracer in a sand and gravel aquifer has been reported by Wood and Ehrlich (1978/T8.5). Yeast is a single-celled fungus that is ovoid in shape. The diameter of a yeast cell is 2 to 3 µm, which closely approximates the size of pathogenic bacterial cells. This tracer is probably most applicable in providing information concerning the potential movement of bacteria.

⁴⁸ Keys, W.S. and R.F. Brown. 1978. The Use of Temperature Logs to Trace the Movement of Injected Water. *Ground Water* 16(1):32–48.

⁴⁹ Rorabaugh, M.I. 1956. Ground Water in Northeastern Louisville, Kentucky. U.S. Geological Survey Water Supply Paper 1360B:101–169.

⁵⁰ Arandjelovic, D. 1969. A Possible Way of Tracing Groundwater Flows in Karst. *Geophysical Prospecting* 17(4):404–418.

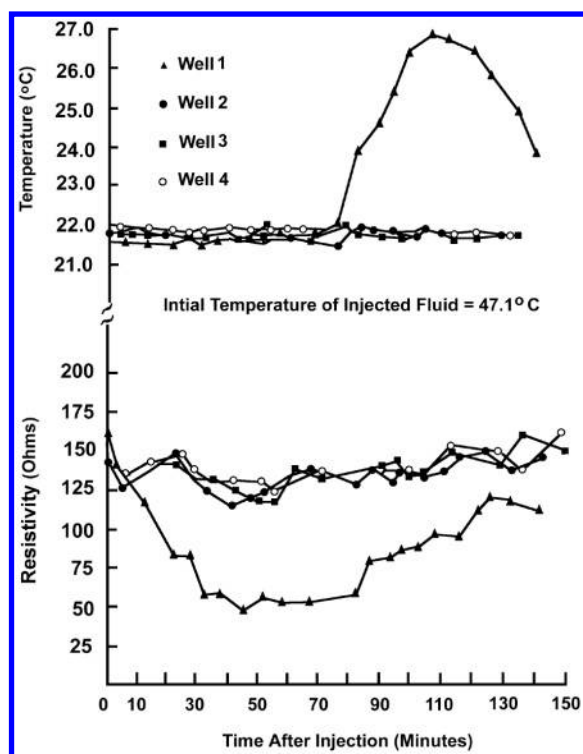


Figure 8.6 Results of field test using a hot water tracer (Boulding, 1991, after Davis et al., 1985).

Table 8.5 Comparison of Microbial Tracers

Tracer	Size (µm)	Time Required for Assay (days)	Essential Equipment Required
Bacteria	1–10	1–2	Incubator ^a
Spores	25–33	1/2	Microscope
Yeast	2–3	1–2	Plankton nets
Viruses:			Incubator ^a
Animal (enteric)	0.2–0.8	3–5	Incubator
			Tissue culture
			Laboratory
Bacterial	0.2–1.0	1/2–1	Incubator* ^a

^a Many may be assayed at room temperature.

Source: Boulding (1991), after Keswick et al. (1982).

Wood and Ehrlich (1978/T8.5) found that the yeast penetrated more than 7 m into a sand and gravel aquifer in less than 48 h after injection. This tracer is very inexpensive, as is analysis. The lack of environmental concerns related to this tracer is another advantage.

Bacteria. Bacteria are the most commonly used microbial tracers, due to their ease of growth and simple detection. Keswick et al. (1982/T8.5) reviewed over 20 case studies of bacteria used as tracers. Some bacteria that have been used successfully are *Escherichia coliform* (*E. coli*), *Streptococcus faecalis*, *Bacillus stearothermophilus*, *Serratia marcescens*, and *Serratia indica*. They range in size from 1 to 10 µm and have been used in a variety of applications.

A fecal coliform, *E. coli*, has been used to indicate fecal pollution at pit latrines, septic fields, and sewage disposal sites. A marker such as antibiotic resistance or H₂S production is necessary to distinguish the tracer from background organisms.

The greatest health concern in using these tracers is that the bacteria must be nonpathogenic to humans. Even *E. coli* has strains that can be pathogenic. Davis et al. (1970) and Wilkowske et al. (1970) have reported that *Serratia marcescens* may be life threatening to patients who are hospitalized with other illnesses.⁵¹ Antibiotic-resistant strains are another concern, as the antibiotic resistance can be transferred to potential human pathogens. This can be avoided by using bacteria that cannot transfer this genetic information. As is true with most other injected tracers, permission to use bacterial tracers should be obtained from the proper federal, state, and local health authorities.

Viruses. Animal, plant, and bacterial viruses have been used as ground-water tracers. Viruses are generally much smaller than bacteria, ranging from 0.2 to 1.0 μm (see Table 8.4). In general, human enteric viruses cannot be used due to disease potential, although certain vaccine strains, such as a type of poliovirus, have been used but are considered risky. Most animal enteric viruses are considered safer, as they are not known to infect humans (Keswick et al., 1982/T8.5). However, neither human nor most animal viruses are generally considered suitable tracers for fieldwork because of their potential to infect humans.

Spores. *Lycopodium* spores have been widely used as tracers in karst hydrogeologic systems in Europe since the early 1950s and have been less frequently used in the U.S. since the 1970s. Much of the literature on the use of spores, however, is in obscure European and American speleological journals. More readily accessible references on the use of spores include Atkinson et al. (1973) and Gardner and Gray (1976).⁵²

Lycopodium is a club moss that has spores nearly spherical in shape, with a mean diameter of 33 μm . It is composed of cellulose and is slightly denser than water, so that some turbulence is required to keep the material in suspension. Some advantages of using *Lycopodium* spores as a tracer are:

- The spores are relatively small.
- They are not affected by water chemistry or adsorbed by clay or silt.
- They travel at approximately the velocity of the surrounding water.
- The injection concentration can be very high (e.g., 8×10^6 spores per cm^3).
- They pose no health threat.
- The spores are easily detectable under the microscope.
- At least five dye colors may be used, allowing five tracings to be conducted simultaneously in a karst system.

Some disadvantages associated with the use of *Lycopodium* spores include the large amount of time required for their preparation and analysis and the problem of spores being filtered by sand or gravel if flow is not sufficiently turbulent.

The basic procedure involves adding a few kilograms of dyed spores to a cave or sinking stream. The movement of the tracer is monitored by sampling downstream in the cave or at a spring with plankton nets installed in the streambed. The sediment caught in the net is concentrated and treated to remove organic matter. The spores are then examined under the microscope.

Tracing by *Lycopodium* spores is most useful in open joints or solution channels (karst terrane) where there is minimal suspended sediment. It is not useful in wells or boreholes unless the water is pumped continuously to the surface and filtered. The spores survive well in polluted water, but do not perform well in slow flow or in water with a high sediment concentration. A velocity of a few miles per hour has been found sufficient to keep the spores in suspension. According to Smart

⁵¹ Davis, J.T., E. Flotz, and W.S. Blakemore. 1970. *Serratia marcescens*, a Pathogen of Increasing Clinical Importance. Journal of the American Medical Association 214(12):2190–2192.

Wilkowske, C.J., J.A. Washington II, W.J. Martin, and R.E. Ritts, Jr. 1970. *Serratia marcescens*: Biochemical Characteristics, Antibiotic Susceptibility and Clinical Significance. Journal of the American Medical Association 214(12):2157–2162.

⁵² Atkinson, T.C., D.I. Smith, J.J. Lavis, and R.J. Whitaker. 1973. Experiments in Tracing Underground Waters in Limestones. Journal of Hydrology 19:323–349.

Gardner, G.D. and R.E. Gray. 1976. Tracing Subsurface Flow in Karst Regions Using Artificially Colored Spores. Association of Engineering Geologists Bulletin 13:177–197.

and Smith (1976),⁵³ *Lycopodium* is preferable to dyes for use in large-scale water resource reconnaissance studies in karst areas. This is true if skilled personnel are available to sample and analyze the spores and a relatively small number of sampling sites are used.

8.4 TRACER TESTS IN KARST AND FRACTURED ROCK

Probably no hydrogeologic system has been more extensively studied by a more diverse group of people with such a plethora of tracing techniques as karst limestone terranes. Geese, tagged eels, computer punch-card confetti, and time bombs are among the more exotic tracers that have been used in karst.

There is an extensive international literature on karst tracing. [Table 8.6](#) identifies major sources of information on this topic. There is a substantial English language literature in American caving journals, such as *Cave Notes/Caves and Karst* (which ceased publication in 1973), *Missouri Speleology*, and the *National Speleological Society Bulletin*, and similar British periodicals, such as *Transactions of the Cave Research Group* (now *Cave Science*) and the *Proceedings of the University of Bristol Speleological Society*. The international symposia on underground water tracing (SUWT) (see [Table 8.6](#)) provide the best systematic compilations of international research on this topic. Probably the easiest way to monitor the international literature on dye tracing in karst terranes and other karst and speleological literature is the annual *Speleological Abstracts* published by the Union Internationale de Spéléologie in Switzerland.

Fluorescent dyes are usually the tracer of choice in karst studies because adsorption is usually not a problem in karst hydrogeologic systems. Smart (1985)⁵⁴ lists four applications of fluorescent dye tracers in evaluating existing or potential contamination in carbonate rocks: (1) confirmation of leachate contamination, (2) determination of on-site hydrology, (3) determination of hydraulic properties of landfill materials, and (4) prediction of leachate contamination and dilution.

Fluorescein, Rhodamine WT, optical brighteners (Tinopal 5BM GX), and Direct Yellow 96 are the most commonly used dyes. The amount of dye injected depends on whether qualitative or quantitative analysis is planned. *Qualitative* tests involve simple visual detection of dye in flowing water or captured by a detector (see discussion below). *Semiquantitative* results can be obtained by using a fluorometer or spectrofluorometer to detect amounts of dye captured by detectors such as activated charcoal that may not be discernable to the eye. Interpretation of values from such measurements is limited due to lack of precise information on the variation in ground-water flow and dye concentration between collection of detectors. *Quantitative* tests involve precise measurement of dye concentrations in a grab sample of water. If the exact amount of injected dye is known, and flow measurements are taken along with each sample, a mass-balance analysis allows estimation of how much dye has been distributed through different parts of the subsurface flow system.

In qualitative tests enough dye must be injected for visual detection; quantitative tests using a fluorometer or spectrofluorometer generally require one tenth to one hundredth as much dye. Determination of the correct quantity to inject is as much an art as a science, and this should be determined by, or with the assistance of, someone with experience in karst tracer tests.

Dye is recovered with detectors called *bugs* (cotton or activated charcoal, depending on the tracer — see [Section 8.3.2](#)) that are typically suspended in streams and springs on hydrodynamically stable stands called *gumdrops*. Detectors are placed at springs or in streams where flow from the point of injection is suspected of reaching the surface. At chosen time intervals related to the distance from the source of injection, detectors are collected and replaced with fresh detectors. Detectors are usually collected frequently during the first few days after injection to pinpoint the most rapid dye arrival time, and then typically on a daily basis for several weeks. Background tests

⁵³ Smart, P.L. and D.I. Smith. 1976. Water Tracing in Tropical Regions: The Use of Fluorometric Techniques in Jamaica. *Journal of Hydrology* 30:179–195.

⁵⁴ Smart, P.L. 1985. Applications of Fluorescent Dye Tracers in the Planning and Hydrological Appraisal of Sanitary Landfills. *Quarterly Journal of Engineering Geology* (London) 18:275–286.

must always be run before injection, especially with optical brighteners, because sewage effluent from individual septic tank absorption fields may increase background levels substantially.

Qualitative tracer tests in which two dyes are injected into two different locations are readily done by combining a fluorescent dye and an optical brightener, which use different detectors. Quantitative techniques are available (developed originally in Europe) for separating mixtures of fluorescent dyes. A five-dye tracer test has recently been conducted using these techniques (see footnote 31). Perhaps the most comprehensive karst tracing experiments in a single location were carried out in Slovenia, Yugoslavia, in the early 1970s where five dyes — *Lycopodium* spores, lithium chloride, potassium chloride, chromium-51, and detergents — were used (Gospodaric and Habic, 1976/T8.5).

Reports prepared for U.S. EPA by Mull et al. (1988/T8.5) and Quinlan (1989/T8.5) are the most comprehensive references currently available on procedures for dye tracing in karst terranes. Smoot et al. (1987/T8.5) and Smart (1988a/T8.5) describe quantitative dye-tracing techniques in karst, and Smart (1988b/T8.5) describes an approach to the structural interpretation of ground-water traces in karst terrane. [Table 8.6](#) also identifies a number of references on the use of tracers for fracture characterization in limestone and other rock types.

8.5 TRACER TESTS IN POROUS MEDIA

Tracer tests in porous media are used primarily to characterize aquifer parameters such as regional velocity (Leap, 1985),⁵⁵ hydraulic conductivity distributions (Molz et al., 1988),⁵⁶ anisotropy (Kenoyer, 1988),⁵⁷ dispersivity (Bumb et al., 1985),⁵⁸ and distribution coefficient or retardation (Pickens et al., 1981; Rainwater et al., 1987).⁵⁹ Smart et al. (1988/T8.5) have prepared an annotated bibliography on ground-water tracing that focuses on use of tracers in porous media.

The purpose and practical constraints of a potential tracer test must be clearly understood prior to actual planning. Following are a few of the questions that need to be addressed:

- Is only the direction of water flow to be determined?
- Are other parameters such as travel time, porosity, and hydraulic conductivity of interest?
- How much time is available for the test?
- How much money is available for the test?

If results must be obtained within a few weeks, then certain kinds of tracer tests would normally be out of the question. Those using only the natural hydraulic gradient between two wells that are more than about 20 m apart typically require long periods for the tracer to flow between the wells. Another primary consideration is budget. Costs for tests that involve drilling of several deep holes, setting of packers to control sampling or injection, and analysis of hundreds of samples in an EPA-certified laboratory could easily exceed \$1 million. In contrast, some short-term tracer tests may be possible at costs of less than \$1000.

⁵⁵ Leap, D.I. 1985. A Simple, Two-Pulse Tracer Method for Estimating Steady-State Ground Water Parameters. *Hydrological Science and Technology: Short Papers* 1(1):37–43.

⁵⁶ Molz, F.J., O. Güven, J.G. Melville, J.S. Nohrstedt, and J.K. Overholzer. 1988. Forced-Gradient Tracer Tests and Inferred Hydraulic Conductivity Distributions at the Mobile Site. *Ground Water* 26(5):570–579.

⁵⁷ Kenoyer, G.J. 1988. Tracer Test Analysis of Anisotropy in Hydraulic Conductivity of Granular Aquifers. *Ground Water Monitoring Review* 8(3):67–70.

⁵⁸ Bumb, A.C., J.I. Drever, and C.R. McKee. 1985. *In Situ* Determination of Dispersion Coefficients and Adsorption Parameters for Contaminations Using a Pull-Push Test. In: *Proceedings of the 2nd International Conference on Ground Water Quality Research* (Oklahoma), N.N. Durham and A.E. Redelfs (eds.), Oklahoma State University Printing, Norman, OK, pp. 186–190.

⁵⁹ Pickens, J.F., R.E. Jackson, K.J. Inch, and W.F. Merritt. 1981. Measurement of Distribution Coefficients Using Radial Injection Dual-Tracer Tests. *Water Resources Research* 17:529–544.

Rainwater, K.A., W.R. Wise, and R.J. Charbeneau. 1987. Parameter Estimation through Groundwater Tracer Tests. *Water Resources Research* 23:1901–1910.

Choice of a tracer will depend partially on which analytical techniques are easily available and which background constituents might interfere with these analyses. The chemist or technician who will analyze the samples can advise whether background constituents might interfere with the analytical techniques to be used. Bacteria, isotopes, and ions are the most frequently used types of tracers in porous media. Fluorescent dyes are less commonly used as tracers because of their tendency to adsorb. A more common use of dyes in porous media is to locate zones of preferential flow in the vadose zone. In this application, adsorption on soil particles is desirable because it allows visual inspection of flow patterns when the soil is excavated.

8.5.1 Estimating the Amount of Tracer to Inject

The amount of tracer to inject is based on the natural background concentrations, the detection limit for the tracer, the dilution expected, and experience. Adsorption, ion exchange, and dispersion will decrease the amount of tracer arriving at the observation well, but recovery of the injected mass is usually not less than 20% for two-hole tests using a forced recirculation system and conservative tracers. The concentration should not be increased so much that density effects become a problem. Lenda and Zuber (1970)⁶⁰ presented graphs that can be used to estimate the approximate quantity of tracer needed. These values are based on estimates of the porosity and dispersion coefficient of the aquifer.

8.5.2 Single-Well Techniques

Two techniques, *injection/withdrawal* and *borehole dilution*, produce parameter values from a single well that are valid at a local scale. Advantages of single-well techniques are:

- Less tracer is required than is for two-well tests.
- The assumption of radial flow is generally valid, so natural aquifer velocity can be ignored, making solutions easier.
- Knowledge of the exact direction of flow is not necessary.

Molz et al. (1985)⁶¹ describe design and performance of single-well tracer tests conducted at the Mobile site.

Injection/Withdrawal. The single-well injection/withdrawal (or pulse) technique results in a pore velocity value and a longitudinal dispersion coefficient. The method assumes that porosity is known or can be estimated with reasonable accuracy. In this procedure, a given quantity of tracer is instantaneously added to the borehole, the tracer is mixed, and then two to three borehole volumes of fresh water are pumped in to force the tracer to penetrate the aquifer. Only a small quantity is injected so as not to disturb natural flow.

After a certain time, the borehole is pumped out at a constant rate large enough to overcome the natural ground-water flow. Tracer concentration is measured with time or pumped volume. If the concentration is measured at various depths with point samplers, the relative permeability of layers can be determined. The dispersion coefficient is obtained by matching experimental breakthrough curves with theoretical curves based on the general dispersion equation. A finite difference method is used to simulate the theoretical curves (Fried, 1975).⁶²

Fried concluded that the method is useful for local information (2- to 4-m radius) and for detecting the most permeable strata. A possible advantage of this test is that nearly all of the tracer is removed from the aquifer at the end of the test.

⁶⁰ Lenda, A. and A. Zuber. 1970. Tracer Dispersion in Groundwater Experiments. In: Proceedings of the IAEA Symposium on Isotope Hydrology, International Atomic Energy Agency, Vienna, pp. 619–641.

⁶¹ Molz, F.J., J.G. Melville, O. Güven, R.D. Crocker, and K.T. Matteson. 1985. Design and Performance of Single-Well Tracer Tests at the Mobile Site. Water Resources Research 21:1497–1502.

⁶² Fried, J.J. 1975. Groundwater Pollution: Theory, Methodology Modeling, and Practical Rules. Elsevier, New York.

Borehole Dilution. This technique, also called *point dilution*, can be used to measure the magnitude and direction of horizontal tracer velocity and vertical flow (Klotz et al., 1978).⁶³

The procedure is to introduce a known quantity of tracer instantaneously into the borehole, mix it well, and then measure the concentration decrease with time. The tracer is generally introduced into an isolated volume of the borehole using packers. Radioactive tracers have been most commonly used for borehole dilution tests, but other tracers can be used.

Factors to consider when conducting a point dilution test include the homogeneity of the aquifer, effects of drilling (mudcake, etc.), homogeneity of the mixture of tracer and well water, degree of tracer diffusion, and density effects.

Ideally, the test should be conducted using a borehole with no screen or gravel pack. If a screen is used, it should be next to the borehole because dead space alters the results. Samples should be very small in volume so that flow is not disturbed by their removal.

A variant of the point dilution method allows measurement of the direction of ground-water flow. In this procedure, a section of the borehole is usually isolated by packers, and a tracer (often radioactive) is introduced slowly and without mixing. Then, after some time, a compartmental sampler (four to eight compartments) within the borehole is opened. The direction of minimum concentration corresponds to the flow direction. A similar method is to introduce a radioactive tracer and subsequently measure its adsorption on the borehole or well screen walls by means of a counting device in the hole. Gaspar and Oncescu (1972/T8.5) describe the method in more detail.

Another common strategy is to inject and subsequently remove the water containing a conservative tracer from a single well. If injection is rapid and pumping to remove the tracer follows immediately, then almost all of the injected conservative tracer can be recovered. If the pumping is delayed, the injected tracer will drift downgradient with the general flow of the ground water and the percentage of tracer recovery will decrease with time. Successive tests with increasingly longer delay times between injection and pumping can be used to estimate ground-water velocities in permeable aquifers with moderately large hydraulic gradients.

8.5.3 Two-Well Techniques

There are two basic approaches to using tracers with multiple wells: one measures tracer movement in uniform (natural) flow, and the other measures movement by radial (induced) flow. The parameters measured (dispersion coefficient and porosity) are assumed to be the same for both types of flow.

Uniform Flow. This approach involves placing a tracer in one well without disturbing the flow field, and sampling periodically to detect the tracer in observation wells. This test can be used at a local (2 to 5 m) or intermediate (5 to 100 m) scale, but it requires much more time than radial tests. If the direction and magnitude of the velocity are not known, a large number of observation wells are needed. Furthermore, local flow directions may diverge widely from directions predicted on the basis of widely spaced water wells. Failure to intercept a tracer in a well just a few meters away from the injection well is not uncommon under natural gradient flow conditions.

The quantity of tracer needed to cover a large distance can be expensive. On a regional scale, environmental tracers, including seawater intrusion, radionuclides, or stable isotopes of hydrogen and oxygen, are used. Man-made pollution has also been used. For regional problems, a mathematical model is calibrated with concentration vs. time curves from field data and is used to predict future concentration distributions.

Local- or intermediate-scale uniform flow problems can be solved analytically, semianalytically, or by curve matching. Layers of different permeability can cause distorted breakthrough curves, which can usually be analyzed using one- or two-dimensional models (Gaspar and Oncescu,

⁶³ Klotz, D., H. Moser, and P. Trimborn. 1978. Single-Borehole Techniques, Present Status and Examples of Recent Applications. In: Proceedings of the IAEA Symposium on Isotope Hydrology, Part 1, International Atomic Energy Agency, Vienna, pp. 159–179.

1972/T8.5). Fried (1975 — footnote 62) and Lenda and Zuber (1970 — footnote 60) present analytical solutions.

Radial Flow. Radial flow techniques work by altering the flow field of an aquifer by pumping. Solutions are generally easier if radial flow velocity greatly exceeds uniform flow. This method yields values for porosity and the dispersion coefficient, but not natural ground-water velocity. Types of radial flow tests include diverging, converging, and recirculating tests.

A *diverging* test involves constant injection of water into an aquifer. The tracer is introduced into the injected water as a slug or continuous flow, and the tracer is detected at an observation well that is not pumping. Point or integrated samples of small volume are carefully taken at the observation well so that flow is not disturbed. Packers can be used in the injection well to isolate an interval.

In a *converging* test, the tracer is introduced at an observation well, while another well is pumped. Concentrations are monitored at the pumped well. The tracer is often injected between two packers or below one packer; then two to three well-bore volumes are injected to push the tracer out into the aquifer. At the pumping well, intervals of interest are isolated (particularly in fractured rock), or an integrated sample is obtained.

A *recirculating* test is similar to a converging test, but the pumped water is injected back into the injection well. This tests a significantly greater part of the formation because the wells inject to and pump from 360°. The flow lines are longer, however, partially canceling out the advantage of a higher gradient. Sauty (1980)⁶⁴ provides theoretical curves for recirculating tests.

8.5.4 Divergent-Line-Drive Techniques

The divergent-line-drive well technique involves injecting tracers in a well field designed to allow tracer flow in two directions, opposite one another from the injection well. The primary purpose of a divergent-line-drive approach is to increase the swept pore volume from a single injection. This allows a greater volume of the subsurface to be swept in a given period and serves to increase the tracer sweep efficiency.

Using a single-line-drive approach, it is often necessary to install hydraulic-control wells where clean water is injected upstream from the injection well(s). By using a divergent-line-drive well pattern, the hydraulic containment of the injected fluids, or solubilized contaminants, can be maximized. Also, dilution of the injected fluids is minimized. A divergent-line-drive technique also minimizes the potential for stagnant flow zones between the wells.

8.5.5 Design and Construction of Test Wells

In many tracer tests, construction of the test wells is the single greatest expense. Procedures for the proper design and construction of monitoring wells for sampling ground-water quality (Section 9.3) apply equally to wells used for tracer tests.

Special considerations in designing and constructing test wells for tracer tests include the following:

- Drilling muds and mud additives tend to have a high capacity for the sorption of most types of tracers and therefore should be avoided.
- Drilling methods that alter the hydrologic characteristics of the aquifer being tested (such as clogging of pores) should be avoided.
- Use of packers to isolate the zones being sampled from the rest of the water in the well (see [Figure 8.2b](#)) allows the most precise measurements of vertical variations in hydrologic parameters. This approach tends to be more expensive, takes longer, and requires more technical training than whole-well tests.

⁶⁴ Sauty, J.P. 1980. An Analysis of Hydrodispersive Transfer in Aquifers. *Water Resources Research* 16(1):145–158.

- Well casing material should not be reactive with the tracer used.
- If packers are not used, the diameter of the sampling well should be as small as possible in order to minimize the amount of “dead” water in the well during sampling.
- Well screen slot size and gravel pack must be selected and installed with special care when using single-well tests with alternating cycles of injection and pumping large volumes of water into and out of loose fine-grained sand. On the other hand, if the aquifer being tested contains very permeable coarse gravel and the casing diameter is small, then numerous holes drilled in the solid casing may be adequate.
- As with any monitoring well, tracer test wells should be properly developed to remove silt, clay, drilling mud, and other materials that would prevent free movement of water in and out of the well.

8.5.6 Injection and Sample Collection

Choice of injection equipment depends on the depth of the borehole and the funds available. In very shallow holes, the tracer can be lowered through a tube, placed in an ampule that is lowered into the hole and broken, or just poured in. Mixing of the tracer with the aquifer water is desirable and important for most types of tests and is simple for very shallow holes. For example, a plunger can be surged up and down in the hole or the tracer can be released through a pipe with many perforations. Flanges on the outer part of the pipe will mix the tracer as the pipe is raised and lowered. For deeper holes, tracers must be injected under pressure and equipment can be quite sophisticated.

Sample collection also can be simple or sophisticated. For tracing thermal pulses, only a thermistor needs to be lowered into the ground water. For chemical tracers, a variety of sampling methods may be used (Section 9.5). Some special sampling considerations for tracer tests include:

- Bailers should not be used if mixing of the tracer in the borehole is to be avoided.
- Where purging is required, removal of more than the minimum required to obtain fresh aquifer water may create a gradient toward the well and distort the natural movement of the tracer (Section 9.5.3).
- Use of existing water wells that tap multiple aquifers should be generally avoided in tracer tests except to establish whether a hydrologic connection with the point of injection exists.

8.5.7 Interpretation of Results

The basic plot of the concentration of a tracer as a function of time or water volume passed through the system is called a *breakthrough curve*. The concentration is plotted either as the actual concentration (Figure 8.7) or, quite commonly, as the ratio of the measured tracer concentration at the sampling point, C , to the input tracer concentration, C_0 (Figure 8.8).

The measured quantity that is fundamental for most tracer tests is the first arrival time of the tracer as it goes from an injection point to a sampling point. The first arrival time conveys at least two bits of information. First, it indicates that a connection for ground-water flow actually exists between the two points. For many tracer tests, particularly in karst regions, this is all the information that is desired. Second, if the tracer is conservative, the maximum velocity of ground-water flow between the two points may be estimated.

Interpretations more elaborate than the two mentioned above depend very much on the type of aquifer being tested, the velocity of ground-water flow, the configuration of the tracer injection and sampling systems, and the type of tracer or mixture of tracers used in the test.

The value of greatest interest after the first arrival time is the arrival time of the peak concentration for a slug injection or, for a continuous feed of tracers, the time since injection when the concentration of the tracer changes most rapidly as a function of time (Figure 8.8). In general, if conservative tracers are used, this time is close to the theoretical travel time of an average molecule of ground water traveling between the two points.

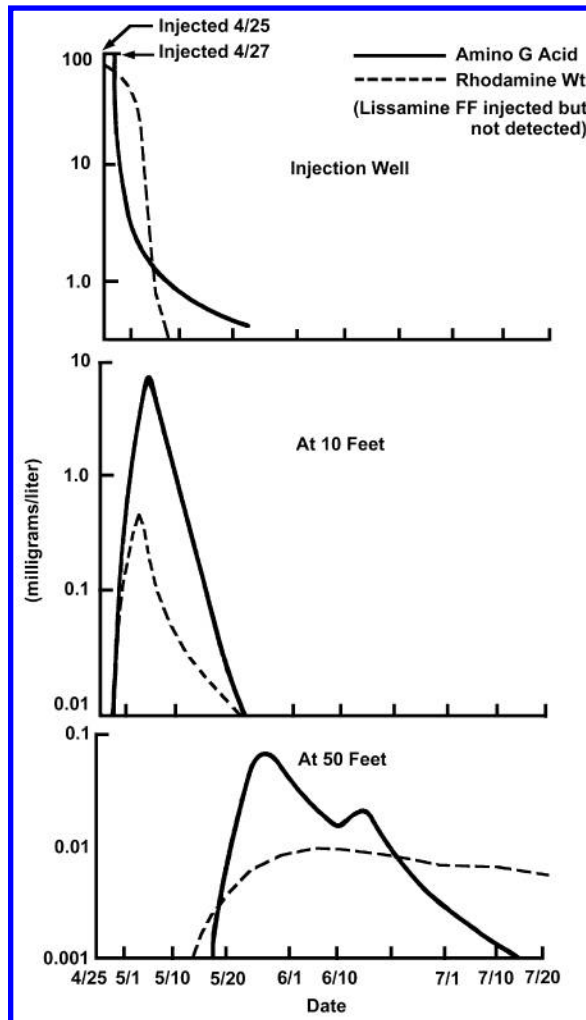


Figure 8.7 Results of tracer tests at the Sand Ridge State Forest, Illinois (Davis et al., 1985, after Naymik and Sievers, 1983).

If a tracer is being introduced continuously into a ditch penetrating an aquifer, as shown in Figure 8.8, then the ratio C/C_0 will approach 1.0 after the tracer starts to pass the sampling point. The ratio of 1.0 is rarely approached in most tracer tests in the field, however, because waters are mixed by dispersion and diffusion in the aquifer and because wells used for sampling will commonly intercept far more ground water than has been tagged by tracers (Figure 8.9). Ratios of C/C_0 ranging between 10^{-5} and 2×10^{-1} are often reported from field tests.

If a tracer is introduced passively into an aquifer but is recovered by pumping a separate sampling well, then various mixtures of the tracer and the native ground water will be recovered depending on the amount of water pumped, the transmissivity of the aquifer, the slope of the water table, and the shape of the tracer plume. Keely (1984)⁶⁵ has presented this problem graphically with regard to the removal of contaminated water from an aquifer.

With the introduction of a mixture of tracers, possible interactions between the tracers and the solid part of the aquifer may be studied. If interactions take place, they can be detected by comparing breakthrough curves of a conservative tracer with the curves of the other tracers being tested (Figure

⁶⁵ Keely, J.F. 1984. Optimizing Pumping Strategies for Contaminant Studies and Remedial Actions. Ground Water Monitoring Review 4(3):63–74.

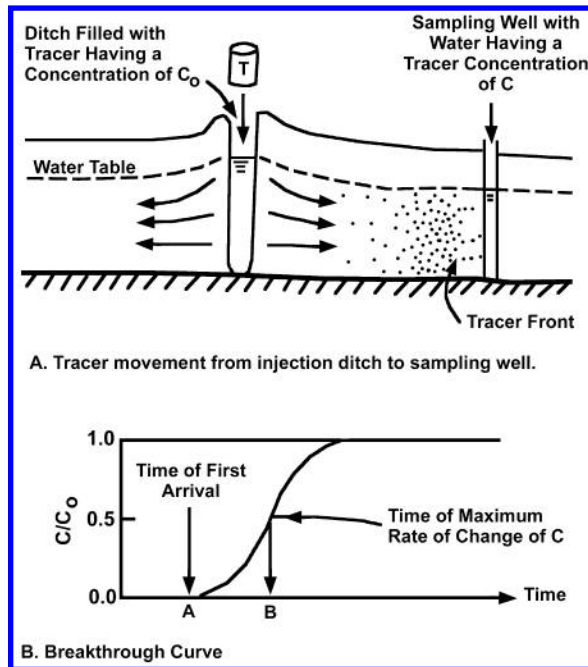


Figure 8.8 Tracer concentration reported as a ratio (Boulding, 1991, after Davis et al., 1985).

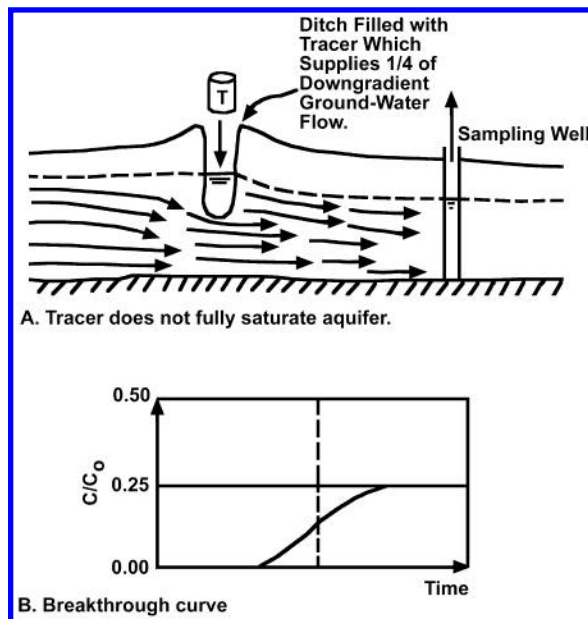


Figure 8.9 Incomplete tracer recovery due to partial penetration of aquifer (Boulding, 1991, after Davis et al., 1985).

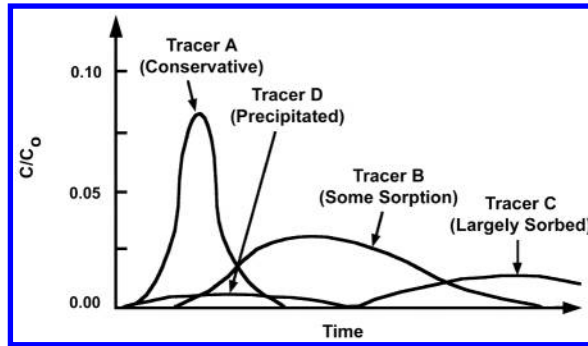


Figure 8.10 Breakthrough curves for conservative and nonconservative tracers (Boulding, 1991, after Davis et al., 1985).

8.10). Quantitative analyses of tracer breakthrough curves are generally by curve matching of computer-generated type curves or by analytical methods.

8.6 GUIDE TO MAJOR REFERENCES

[Table 8.6](#) identifies major references on tracer methods in the following areas: (1) general reviews and bibliographies, (2) specific tracers, (3) karst tracing, and (4) interpretations.

Three good general references on the use of fluorescent dyes are three U.S. Geological Survey publications (Hubbard et al., 1982; Kilpatrick and Cobb, 1985; Wilson et al., 1986). [Section 8.4](#) provides an overview of major sources of information on tracing in karst systems. Two reports prepared for U.S. EPA (Mull, 1988; Quinlan, 1989) are the best recent sources on practical aspects of dye tracing in karst areas.

Because microbial contamination is a widespread and significant contaminant, [Table 8.6](#) contains a number of journal references involving site-specific cases in addition to general reviews.

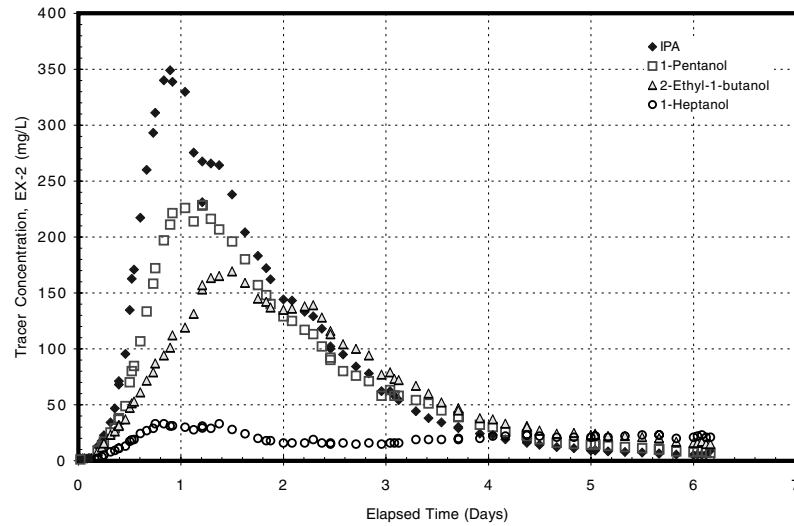


Figure 8.11a Example breakthrough curves for partitioning tracers applied before remediation (Londergan et al., 2001).

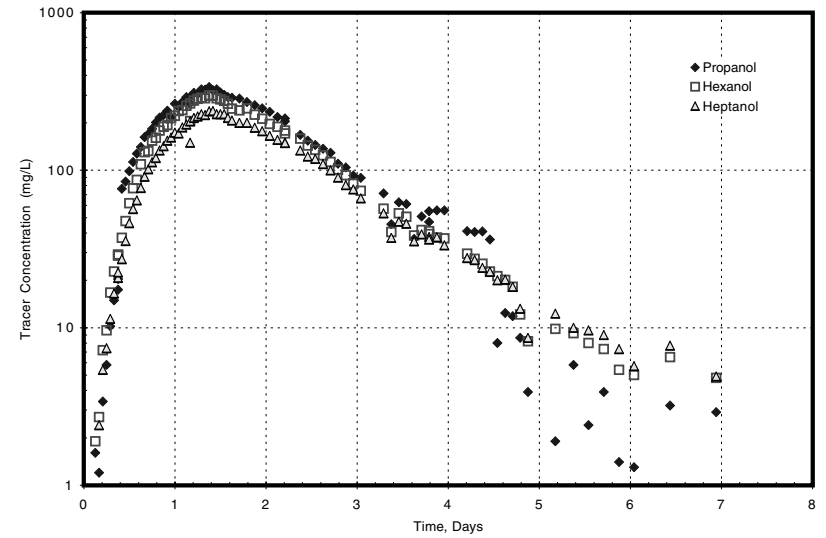


Figure 8.11b Example breakthrough curves for partitioning tracers applied after remediation (Londergan et al., 2001).

Table 8.6 Index to Major References on Soil and Ground Water Tracer Methods

Topic	References
General Reviews	<u>Texts</u> : Gaspar (1987), Käss (1998); <u>Other</u> : AGWSE (1989), Atkinson and Smart (1981), Aulenbach et al. (1978), Davis et al. (1980, 1985), Drew and Smith (1969), Everts et al. (1979), Grisak et al. (1983), Knuttsen (1968), Molz et al. (1986, 1987), U.S. EPA (1991 — Chapter 4)
Bibliographies	Edwards and Smart (1988a, 1988b), LaMoreaux et al. (1984, 1989), Smart et al. (1988), Taylor and Dey (1985), van der Leeden (1991)
Specific Tracers	
Dyes	Drew and Smith (1969), Feuerstein and Selleck (1963), Hubbard et al. (1982), Kilpatrick and Cobb (1985), McLaughlin (1982), Mull et al. (1988), Quinlin (1989), Smart and Laidlaw (1977), Thrailkill et al. (1983), Wilson et al. (1986); <u>Toxicity</u> : Field et al. (1990), Smart (1984); <u>Quantitative Interpretations</u> : Brown and Ford (1971), Smart (1980a, 1980b), Smoot (1991), see also karst tracing
Ionic Tracers	Bowman (1984), Bowman and Gibbons (1992), Kaufman and Orlob (1956a, 1956b), Kaufman and Todd (1955); <u>Single-Well Tests</u> : Hall (1993), Hall et al. (1991), Klotz et al. (1978), Leap (1985), Leap and Kaplan (1988), Molz et al. (1985), Pickens et al. (1981)
Alcohols	<u>Theory and Interpretation</u> : Annable et al. (1998a, 1998b), Brusseau et al. (1999a), Burt et al. (1998), Dwarakanath (1997), Dwarakanath et al. (1999), Jackson et al. (2000), Jin (1995), Jin et al. (1995, 2000), Nelson et al. (1999), Payne et al. (1998), Wilson et al. (2000), Wise (1999)
Microorganisms	<u>Reviews</u> : Crane and Moore (1984), Gerba (1983, 1985, 1987), Gerba and Bitton (1984), Keswick and Gerba (1980), Keswick et al. (1982), Matthess and Pekdeger (1985), Romero (1970), Sobsey and Shields (1987), Vaughn and Landry (1983), Wood and Ehrlich (1978); <u>Bacteria</u> : Allen and Morrison (1973), Caldwell and Morita (1988), Gerba and Goyal (1985), Gerba et al. (1975), Hagedorn (1984), Hagedorn et al. (1978, 1981), Hendricks et al. (1979), Peterson and Ward (1989), Rahe et al. (1978), Robeck (1969), Van Donsel (1967); <u>Viruses</u> : Drewery and Eliassen (1968), Shaffer (1977), Tyler (1985), Vaughn et al. (1981, 1983)
Stable Isotopes	Back and Cherry (1976), Back and Zoetl (1975), Bowen (1980 — Chapter 3), Clark and Fritz (1997), Coleman et al. (1977), Criss (1999), Davis and Bentley (1982), Ehleringer et al. (1993), Faure (1986), Ferronsky and Polyakov (1982), Fritz and Fontes (1980, 1986), Halevy et al. (1967), Hoefs (1980), IAEA (1967a, 1967c, 1970, 1974a, 1974b, 1978a), Lamoreaux et al. (1984), Mazor (1996), Moser and Rauert (1985), Payne (1972, 1988), Pearson et al. (1991), Schimel (1993), Stout (1967), Toran (1982); <u>Nitrogen Isotopes</u> : Knowles and Blackburn (1992)
Radioactive Isotopes	Clark and Fritz (1997), Csallany (1966), Faure (1986), Gaspar and Oncescu (1972), Jäeger and Hunziker (1979), Kaufman and Orlob (1956a, 1956b), Kaufman and Todd (1955), IAEA (1963, 1967b, 1967c, 1968, 1974b, 1978b), Ivanonitch and Harmon (1992), Mather (1968), Thornhill and Benefield (1990), Wiebenga et al. (1967); <u>Carbon Isotopes</u> : Coleman and Fry (1991), Ehleringer et al. (1993); <u>Case Studies</u> : Bradbury (1991 — tritium)
Other	Baker and Lamont-Black (2001 — dissolved organic matter), Mahler et al. (1998 — lanthanide-labeled clay), McKay et al. (2000 — colloids)
Applications	
Karst Tracing	Aley and Fletcher (1976), Bögli (1980), Brown (1972), Ford and Williams (1989), Gospodaric and Habic (1976), LaMoreaux (1984, 1989), Milanović (1981), Mull et al. (1988), Quinlan (1989), Sweeting (1973), SUWT (1966, 1970, 1976, 1981, 1986), Thrailkill et al. (1983); <u>Review Papers</u> : Back and Zoetl (1975), Brown and Ford (1971), Dunn (1957), Gunn (1982), Jones (1984), Smart (1976)
Fracture Characterization	Kerfoot (1992), Lewis et al. (1966), Morin et al. (1988), Tsang (1992)
NAPL Characterization	<u>LNAPL</u> : Annable et al. (1998a, 1998b, 1999), Barcelona and Jaglowski (1999), Bedient et al. (1999), Blanford et al. (1999), Falta et al. (1999), Gierke et al. (1999), Jawitz et al. (1998), Knox et al. (1999), Rao et al. (1997); <u>DNAPL</u> : Brown et al. (1999), Brusseau et al. (1999b), DE&S and Inc. (1999), Dwarakanath (1997), Dwarakanath et al. (1999), Hayden and Linnemeyer (1999), Londergan et al. (2001), Meinardus et al. (1998, 1999, 2000), Nelson and Brusseau (1996), Young et al. (1999)

Table 8.6 Index to Major References on Soil and Ground Water Tracer Methods (Continued)

Topic	References
<u>Interpretation</u>	Bullivant and O'Sullivan (1989), Fried (1975), Grisak and Pickens (1980a, 1980b), Güven et al. (1985, 1986), Halevy and Nir (1962), Molz et al. (1986, 1987), Sauty (1978), Theis (1963)

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Table 8.6 References (Appendix F contains references for figure and table sources.) (*Continued*)

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* See Preface for information on how to obtain documents from CERI and NTIS.

Field Sampling and Monitoring of Contaminants

This chapter focuses on field procedures and devices for sampling and monitoring of contaminants in the vadose zone and ground water. No field sampling or other procedures should be undertaken until a sampling and monitoring plan has been developed for a site (Section 5.3). The information in this chapter may be useful for selection of sampling devices and types of monitoring installations for a sampling and monitoring plan. Field sampling for *site characterization* involves collection of one-time soil-gas, solid, or ground-water samples to define subsurface geology and hydrogeology and the distribution of contaminants. Field sampling for *monitoring* involves the collection of a series of samples at specified locations to evaluate changes in a parameter of interest over time. Monitoring usually involves sampling for chemical analysis, but some physical parameters such as moisture content and matric potential (Section 7.1.1) and ground-water levels (Section 7.2.1) are sufficiently time varying that time-series measurements are useful.

As in Chapter 7 (Characterization of Vadose Zone and Ground Water Hydrology), EPA's guide to *Subsurface Characterization and Monitoring Techniques* (Boulding, 1993/T9.10) is recommended for use as a companion to this chapter for illustrations and more detailed information about specific techniques. Appendix A in this book contains major method summary tables from that guide, which can be used to quickly identify the location of specific methods of interest. Appendix B provides an index and listing of American Society for Testing and Materials (ASTM) standards related to drilling and soil and ground-water sampling methods.

9.1 TYPES OF MONITORING INSTALLATIONS

Subsurface sampling for the purpose of monitoring typically involves placement of access tubes for portable sampling devices or burial of sensors or samplers *in situ*. Installations above the saturated zone monitor are used to monitor soil gas, soil moisture, or soil solutes. Installations below the saturated zone are used to monitor water levels and collect ground-water samples.

9.1.1 Vadose Zone Monitoring Installations

Specific types of installations that can be used for monitoring the potential for contaminant movement in the vadose zone include (1) soil moisture monitoring (Section 7.1.1), (2) soil gas monitoring (Section 9.4.2), and (3) indirect and direct measurements of solute movement (Section 9.4.3). Figure 9.1 illustrates a number of different types of vadose zone monitoring installations for a hazardous waste landfill. Vadose zone monitoring is appropriate for many potential pollution

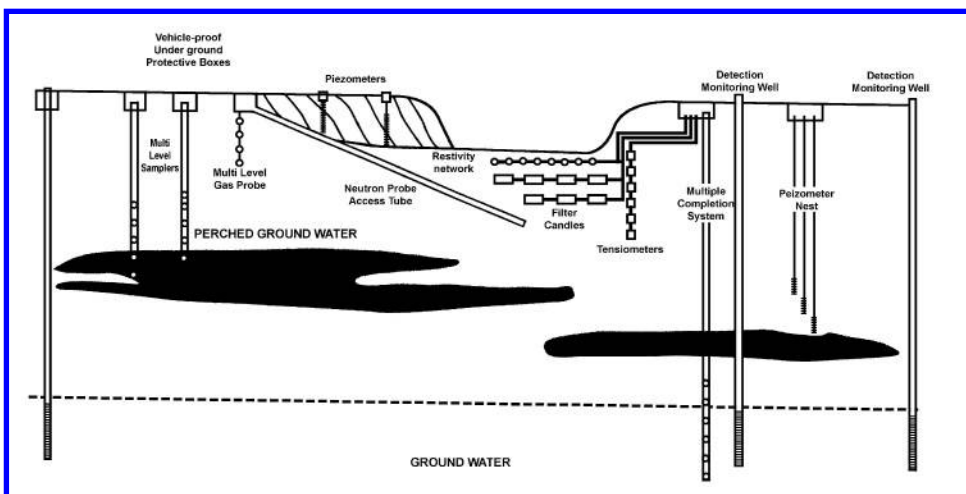


Figure 9.1 Generic monitoring design for existing hazardous waste landfill (Sara, 1994, after Everett et al., 1983).

sources, including sanitary landfills, land treatment facilities, spoil piles, septic tank areas, pits, ponds, lagoons, dry channels used for effluent disposal, and irrigated fields (Wilson, 1981/T6.10).

The U.S. Environmental Protection Agency is placing increasing emphasis on vadose zone soil-solute sampling as an early warning system to detect movement of contaminants before they reach the saturated zone (Cullen, 1995; Durant et al., 1993).¹ Where contaminant sources are located above the saturated zone, and a vadose zone monitoring program indicates no vertical or lateral movement of contaminants, it may be possible to reduce the scope of a ground-water monitoring program. Also, early cleanup of contaminants in the vadose zone may reduce the need for an intensive ground-water monitoring and remediation program. Murdoch et al. (2000)² have developed a device for embedding sensors in the sidewall of a vertical or angled borehole, which greatly enhances the ease with which multilevel monitoring in the vadose zone can be accomplished. The device can also be used to collect soil cores.

9.1.2 Ground Water Monitoring Installations

Table 9.1 summarizes advantages and disadvantages of six major types of monitoring well installations: (1) *single riser with limited screened interval* (commonly 5 to 10 ft), (2) *single riser/long screen* (in which the full thickness of an aquifer is screened), (3) *nested wells in a single borehole* with screens placed at different depths, (4) *nested wells in multiple boreholes* with screens placed at different depths, (5) *multilevel capsule samplers/sensors* placed in a single borehole with tubing rather than casing running to the surface for sample collection, and (6) *multiple port casings* that allow collection of samples at different levels from a single casing. Various hybrid combinations are also possible. The first type (single riser with limited screened interval) alone or as nested wells in multiple boreholes (type 4 above) is generally required at sites where monitoring is required under a federal or state regulatory program such as Superfund (uncontrolled hazardous waste sites) and RCRA (controlled hazardous and nonhazardous disposal sites). These conventional installations are discussed in more detail in [Section 9.3](#).

The installation types described above typically require drilling of a borehole placement of casing or *in situ* samplers and filling of the remaining space with filter pack or grout. Another

¹ Cullen, S.J. 1995. Vadose Zone Monitoring: Experiences and Trends in the United States. *Ground Water Monitoring Review* 15(3):136–143. Durant, N.D., V.B. Myers, and L.A. Eccles. 1993. EPA's Approach to Vadose Zone Monitoring at RCRA Facilities. *Ground Water Monitoring and Remediation* 13(1):151–158.

² Murdoch, L.C., W.W. Slack, W. Harrar, and R.L. Siegrist. 2000. Embedded Sidewall Samplers and Sensors to Monitor the Subsurface. *Ground Water* 38:657–664.

Table 9.1 Advantages and Disadvantages of Types of Monitoring Well Installations

Type	Advantages	Disadvantages
Single-riser/ limited screened interval	<ul style="list-style-type: none"> Simple and suitable for any type of formation Easier to install, pack, and seal than multilevel installations No potential for vertical cross-contamination between sampling points due to leaky seals Maximum flexibility in selection of well diameter (up to diameter of borehole) Most common well diameters (2 to 4 in.) do not restrict the choice of sample collection methods 	<ul style="list-style-type: none"> Provide no information on the vertical distribution of contaminants High cost per sampling point compared to multilevel installations, especially at great depth Contaminant plume might bypass wells with short screened intervals
Single riser/long screen	<ul style="list-style-type: none"> Simple and suitable for any type of formation Easier to install, pack, and seal than multilevel installations Maximum flexibility in selection of well diameter (up to diameter of borehole) Most common well diameters (2 to 4 in.) do not restrict the choice of sample collection methods Where flow-through assumptions apply, there is no need to purge the well before sampling, and the number of vertical sampling points is not limited by the diameter of the well 	<ul style="list-style-type: none"> Do not generally give accurate measurement of maximum concentrations because concentration and hydraulic-head values tend to be averaged over the length of the screen Can cause cross-contamination in an aquifer by connecting contaminated zones to uncontaminated zones; consequently, they can confirm the presence, but not the absence of a contaminant The underlying assumption for flow-through wells that the well screen will not alter the flow of ground water cannot be supported for most natural systems
Nested wells/ single borehole	<ul style="list-style-type: none"> Allow sampling for vertical distribution of ground-water constituents Lower cost per sampling point than separate single-riser wells Generally smaller diameters of individual wells in a nest, compared to single-riser installations, mean that smaller volumes of water must be removed for purging 	<ul style="list-style-type: none"> Installation, packing, and sealing are more difficult than for single-level installations and increase greatly as the number of wells in the boreholes increases Screened intervals must be separated by a grout seal with the possibility that small zones of contaminated water might be missed in heterogeneous materials Cross-contamination of sampling points might occur as a result of leaky seals (this can be checked using tracer tests) Number of sampling points per borehole is restricted by the diameter of the borehole and the diameter of the individual piezometers Bundle piezometers are suitable only where cohesionless sands will collapse around the tips Small diameter of individual piezometers can restrict choice of sampling methods In fine-grained material with low hydraulic conductivity, the small storage volume of individual piezometers might make it difficult to collect samples of sufficient volume
Nested wells/ multiple boreholes	<ul style="list-style-type: none"> Allow sampling for vertical distribution of ground-water constituents Somewhat lower cost per sampling point than widely spaced single-riser wells Simple design and operation Potential for cross-contamination between different levels in the aquifer is eliminated Only the drilling method limits well diameter If desired, screened intervals can be placed to provide complete vertical coverage of the aquifer 	<ul style="list-style-type: none"> More expensive than nested wells in a single borehole Small zones of contaminated water might be missed in heterogeneous materials if the screened intervals do not provide complete vertical coverage of the aquifer

Table 9.1 Advantages and Disadvantages of Types of Monitoring Well Installations (Continued)

Type	Advantages	Disadvantages
Multilevel capsule samplers/sensors	<ul style="list-style-type: none">• Allow sampling for vertical distribution of ground-water constituents• Relatively easy to operate and safer than most other installation types where hazardous contaminants are involved• Minimal purging is required because there is little mixing between incoming water from the formation and stagnant water	<ul style="list-style-type: none">• Proper installation is difficult• Cost per sampling point is moderately high• Depending on type of sampler, number of sampling points might be limited by the diameter of the borehole (commonly three to four sampling points for 6-in. borehole)• Permanent nature of installation means that devices at individual sampling points cannot be retrieved for servicing or repairs, and malfunction means the sampling point is lost• Cross-contamination is a potential concern with multilevel installations requiring grout to isolate sampling points• The choice of sample collection method is restricted to gas-drive or suction-lift devices (for shallow water table)
Multiple port casings	<ul style="list-style-type: none">• Allow sampling for vertical distribution of ground-water constituents• Cost per sampling point is relatively small (except for Westbay system)• Generally smaller diameters of individual wells in a nest, compared to single-riser installations, mean that smaller volumes of water must be removed for purging• Seals between sampling points can be obtained using permanent packers or traditional back-filled seals	<ul style="list-style-type: none">• Assembly and placement can be difficult• Cross-contamination of sampling points possible as a result of leaky seals• The number of sampling points is limited by the diameter of the casing and the tubing that runs to each sample port (does not apply to Westbay system)• Permanent nature of installation means that devices at individual sampling points cannot be retrieved for servicing or repairs, and malfunction means the sampling point is lost• The Westbay system is very expensive, but can be cost-effective if a large number of sampling points at great depth are required• Operation of the Westbay system requires special operator skills and can be time-consuming• The downhole complexity of the Westbay system might result in mechanical difficulties

Source: Adapted from Boulding (1993b).

general type of monitoring well installation involves driving casing with a well point or other type of tip that allows sample collection manually or hydraulically to the desired sampling depth. *Driven well points* have long been used for shallow well installations. *Push technologies*, such as cone penetration rigs and other truck-mounted hydraulic push and vibratory systems that use small-diameter casing (generally 1 in. or less), are being increasingly used for sampling and installation of temporary or permanent monitoring wells in environmental studies (see ASTM D6705/TA.14). Advantages of such installations include (1) lower cost and easy installation, by hand if necessary; (2) the ability to collect water samples as driving proceeds; and, (3) depending on overburden, the achievement of a good seal between casing and formation. Disadvantages include the following: (1) use is limited to fairly soft materials — it is hard to penetrate compact, gravelly materials; (2) it is hard to develop wells; (3) the screen may become clogged if thick clays are penetrated; (4) the requirement for metal casing means that the method is not suitable where contaminant or geochemical conditions require plastic casing; and (5) the sampling device options for depths below the capacity of the suction-lift sampling devices (around 25 ft) are more limited than those for conventional installation because of small casing diameter.

Figure 9.2 illustrates three types of small-diameter monitoring installations using a hydraulically driven filter-tip probe that can be permanently placed in either the vadose zone or the saturated zone for sampling. Table A.8 (driven wells and cone penetration) provides more information about methods using push techniques.

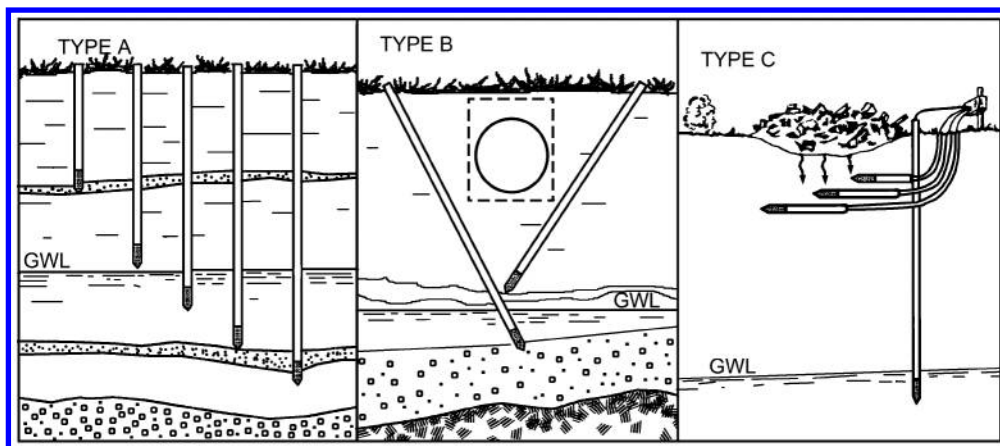


Figure 9.2 Example of permanent installation of BAT filter-tip probe (Torstensson, 1984).

9.2 DRILLING METHODS FOR SAMPLING AND WELL INSTALLATION

Most subsurface investigations require the drilling of boreholes for one or more purposes: (1) collection of solids samples or cores for lithologic logging and laboratory testing, (2) lithologic and hydrogeologic characterization using borehole geophysical logging, and (3) installation of piezometers or monitoring wells.

9.2.1 Selection Criteria

A wide variety of drilling methods have been developed that could be suitable for one or more of the purposes described above. A number of criteria are used when selecting drilling methods, including (1) availability and cost, (2) suitability for the type of geologic materials at a site (unconsolidated or consolidated), (3) maximum depth required for sampling or well installation, (4) whether core samples are required, (5) required diameter for well installations, and (6) potential effects on sample integrity (influenced by drilling fluids and potential for cross-contamination between aquifers).

Table A.8 provides the following information on 20 drilling methods: (1) whether drilling advances in an open hole or with casing, (2) whether fluids used with the method may affect the chemistry of ground-water samples, (3) whether core samples can be taken, and (4) the sections and tables in Boulding (1993/T9.10), where more detailed information about the method can be found.

9.2.2 Auger and Rotary Methods

The most commonly used drilling methods can be broadly classified as *augering* and *rotary* methods. Augering methods include *hollow-stem*, *solid-stem*, and *bucket* augers, with the hollow-stem auger being by far the most commonly used method for well installation in unconsolidated deposits. The Ellog Auger drill has electrical and gamma logging instruments integrated into the hollow-stem auger, and a slotted stem above the cutting head allows collection of soil gas and ground-water samples.³ Rotary drilling methods encompass a wide variety of techniques, most of which involve use of an *air rotary* or *mud rotary* rig. Rotary methods can also be classified according to (1) *open-hole* or *casing* advancement, (2) normal (air or fluid down the drill stem) or *reverse*

³ Sørensen, K. and F. Larsen. 1999. Ellog Auger Drilling: Three-in-One Method for Hydrogeological Data Collection. Ground Water Monitoring and Remediation 19(4):97–101.

circulation (air or fluid up the drill stem), and (3) type of cutting tool (bit, hammer, reamer). Air rotary is probably the most commonly used method for well installation in consolidated formations. A variant of the air rotary method is *cryogenic drilling*, where cold nitrogen rather than ambient air is used as the circulating fluid. This approach can be useful in unstable unconsolidated sediments, or as a means of preventing cross-contamination, by freezing contaminants in place.⁴ Otherwise, where cross-contamination between aquifers is a concern, some kind of casing advancement method is required, with drill-through methods and dual-wall reverse circulation being the most commonly used. Table 9.2 describes major types of auger and rotary methods and summarizes their advantages and disadvantages.

9.2.3 Other Drilling Methods

Table 9.3 provides brief descriptions and the advantages and disadvantages of the following additional drilling methods: (1) sonic drilling, (2) directional drilling, (3) cable tool, (4) jetting and jet percussion, and (5) rotary diamond (which could also be classified as a rotary method). Table A.8 provides additional comparative information on these methods.

Sonic and *directional* drilling have received a lot of recent attention in the context of environmental investigations. Sonic drilling, also called *vibratory* and *rotosonic* drilling, has been experimented with since the 1940s, but recent improvements in equipment design are likely to result in increased use of the method in the future. If further design improvements allow reduction in operating and maintenance costs, sonic drilling could become the method of choice for many settings. Directional drilling, also called *slant rig*, *radial*, and *horizontal* drilling, has also been around for a while, but only relatively recently have applications in environmental investigations received much attention. Slant rig and radial drilling systems were originally developed in the petroleum industry and are relatively expensive. The utility industry has long used less sophisticated (and hence less expensive) directional drilling equipment systems for placement of underground cable, and improvements in this technology are likely to result in increased environmental applications.

Cable tool or *percussion* drilling is commonly used for water well installations, but is less common for monitoring well installations. *Jetting* and *jet percussion* have relatively limited capabilities and are not commonly used for monitoring well installations. The term *wash boring* is also used to describe the jetting method in water well applications and the jet percussion method in geotechnical applications, so when this term is encountered, the operation of the method needs to be examined to determine which method is involved. *Rotary diamond* drilling is commonly used for mineral exploration in crystalline rock, but less commonly for monitoring well installation.

9.3 CONVENTIONAL MONITORING WELL INSTALLATIONS

Monitoring well design involves several components, including casing and screen material, well casing diameter, screen and gravel pack specifications, screen length and depth of placement, and sealing material. Often, the selection of one component will influence the determination of other components. Elements that are factored into the well design aspect of an overall monitoring program include the geologic setting, the results of previous site investigations, well drilling expertise, well logging and aquifer property determinations, regulatory requirements and specifications, details of the history of the site, and the chemical parameters of concern (ASTM 5092/TA.14). Wassenaar and Hendry (1999)⁵ describe special techniques for installation of monitoring wells in very slowly permeable materials.

⁴ Simon, R.D. and G.A. Cooper. 1996. Cryogenic Drilling: A New Drilling Method for Environmental Remediation. *Ground Water Monitoring and Remediation* 16(3):79–85.

⁵ Wassenaar, L.I. and M.J. Hendry. 1999. Improved Piezometer Construction and Sampling Techniques to Determine Pore Water Chemistry in Aquitards. *Ground Water* 37:564–571.

Table 9.2 Advantages and Disadvantages of Auger and Rotary Drilling Methods

Method	Advantages	Disadvantages
Augers		
<p>Hollow and Solid Stem: Successive 5-ft flights of spiral-shaped drill stem are rotated into the ground to create a hole; cuttings are brought to the surface by the turning action of the auger</p>	<ul style="list-style-type: none"> • Inexpensive • Fairly simple operation • Small rigs can get to difficult-to-reach areas • Quick setup time • Can quickly construct shallow wells in firm, noncavey materials • No drilling fluid required • Use of hollow-stem augers greatly facilitates collection of split-spoon samples • Small-diameter wells can be built inside hollow-stem flights when geologic materials are cavey 	<ul style="list-style-type: none"> • Depth of penetration limited, especially in cavey materials • Maximum depth around 150 ft • Cannot be used in rock or well-cemented formations • Difficult to drill in cobbles/boulders • Log of well is difficult to interpret without collection of split spoons due to the lag time for cuttings to reach ground surface • Vertical leakage of water through borehole during drilling is likely to occur • Solid-stem limited to fine-grained, unconsolidated materials that will not collapse when unsupported • With hollow-stem flights, heaving materials can present a problem • May need to add water down auger to control heaving or wash materials from auger before completing well
Rotary Methods		
<p>Direct (Mud) Rotary: Rotating bit breaks formation; cuttings are brought to the surface by a circulating fluid (mud); mud is forced down the interior of the drill stem, out the bit, and up the annulus between the drill stem and hole wall; cuttings are removed by settling in a mud pit at the ground surface, and the mud is circulated back down the drill stem</p>	<ul style="list-style-type: none"> • Drilling is fairly quick in all types of geologic materials • Borehole kept open by formation of a mud wall on sides of borehole by the circulating drilling mud facilitating geophysical logging and well construction • Geologic cores can be collected • Virtually unlimited depths possible 	<ul style="list-style-type: none"> • Expensive; requires experienced driller and fair amount of peripheral equipment • Completed well may be difficult to develop, especially small-diameter wells, because of mud wall on borehole • Geologic logging by visual inspection of cuttings is fair due to presence of drilling mud; thin beds of sand, gravel, or clay may be missed • Presence of drilling mud can contaminate water samples, especially the organic, biodegradable muds • Circulation of drilling fluid through a contaminated zone can create a hazard at the ground surface with the mud pit and cross-contaminate clean zones during circulation
<p>Reverse Rotary: Similar to mud rotary method except the drilling fluid is circulated down the borehole outside the drill stem and is pumped up the inside; water is used as the drilling fluid, rather than a mud, and the hole is kept open by the hydrostatic pressure of the water standing in the borehole</p>	<ul style="list-style-type: none"> • Creates a very “clean” hole, not dirtied with drilling mud • Can be used in all geologic formations • Very deep penetrations possible • Split-spoon sampling possible 	<ul style="list-style-type: none"> • A large water supply is needed to maintain hydrostatic pressure in deep holes and when highly conductive formations are encountered • Expensive; experienced driller and much peripheral equipment required • Hole diameters are usually large, commonly 18 in. or greater • Cross-contamination from circulating water likely • Geologic samples brought to surface are generally poor; circulating water will wash finer materials from sample
<p>Air Rotary: Very similar to mud rotary, the main difference being that air is used as primary drilling fluid as opposed to mud or water</p>	<ul style="list-style-type: none"> • Can be used in all geologic formations; most successful in highly fractured environments • Useful at any depth • Fairly quick • Drilling mud or water not required 	<ul style="list-style-type: none"> • Relatively expensive • Cross-contamination from vertical communication possible • Air will be mixed with water in the hole and that which is blown from the hole, potentially creating unwanted reactions with contaminants; may affect representative samples

Continued.

Table 9.2 Advantages and Disadvantages of Auger and Rotary Drilling Methods (Continued)

Method	Advantages	Disadvantages
Air-Percussion Rotary/Downhole Hammer: Air rotary with a reciprocating hammer connected to the bit to fracture rock	<ul style="list-style-type: none"> • Very fast penetrations • Useful in all geologic formations • Only small amounts of water needed for dust and bit temperature control 	<ul style="list-style-type: none"> • Cuttings and water blown from the hole can pose a hazard to crew and surrounding environment if toxic compounds encountered • Organic foam additives to aid cuttings removal may contaminate samples • Relatively expensive • As with most hydraulic rotary methods, the rig is fairly heavy, limiting accessibility • Vertical mixing of water and air creates cross-contamination potential • Hazard posed to surface environment if toxic compounds encountered • Organic foam additives for cuttings removal may contaminate samples
Rotary Casing Advancement Methods: Various methods (rotary drill-through, reverse dual-wall rotary, downhole casing advancers) involving air or mud rotary with a casing	Varies with specific technique: <ul style="list-style-type: none"> • General advantage is that advancing casing minimizes cross-contamination • Most methods work well in difficult formations, such as unconsolidated materials with boulders, and fractured rock 	Varies with specific technique: <ul style="list-style-type: none"> • Generally more expensive than conventional air and mud rotary

Source: Adapted from Boulding (1993b).

9.3.1 Well Casing and Screens

Conventional monitoring wells are typically 2 in. in diameter, but the increasing availability of small-diameter sampling devices has resulted in a trend toward even smaller diameters (1 to 1.5 in.). Smaller-diameter wells reduce cost of materials and purge volumes. Casing materials can be broadly classified as (1) plastic, (2) metallic, and (3) fiberglass reinforced. [Table 9.4](#) summarizes relative advantages and disadvantages of these materials.

There are two major classes of plastic casing: (1) *thermoplastics*, including polyvinyl chloride (PVC) and acrylonitrile butadiene styrene (ABS), and (2) *fluoropolymers*, including polytetrafluoroethylene/tetrafluoroethylene (PTFE/TFE) (Teflon, Halon, Fluon, Hostafion, Polyflon, Algoflon, Soriflon); fluorinated ethylene propylene (FEP) (Neflon, Teflon); perfluoroalkoxy (PFA) (Neoflon, Teflon); polyvinylidene fluoride (PVDF) (Kynar); and chlorotrifluoroethylene (CTFE) (Kel-F, Diaflon). *PVC* is by far the most commonly used casing material for monitoring wells. Although much research has been published about *PTFE* and other fluoropolymers, actual use is uncommon due to expense and low strength.

Metallic casing types include (1) cast iron, (2) mild or soft steel, (3) carbon steel, (4) low carbon steel, (5) galvanized steel, and (6) stainless steel (particularly types 304 and 316). *Stainless steels* are the most chemically resistant of the ferrous materials and, after PVC, are probably the most commonly used material for monitoring wells. *Fiberglass-reinforced* casings include (1) fiberglass-reinforced epoxy (FRE), and (2) fiberglass-reinforced plastic (FRP). Use of fiberglass-reinforced casings is still largely experimental.

Well *screens* of the appropriate material, length, and slot size are attached to solid casing and placed at the depth in the aquifer where sampling is desired. The *slot size* is selected to (1) maximize the open area for water to flow through, and (2) minimize entry of fines into the well during pumping. The most commonly used types of well intake screens for monitoring well construction are *factory-slotted pipe* (machine cut to uniform width and length around the pipe) and *continuous-*

Table 9.3 Advantages and Disadvantages of Other Drilling Methods

Method	Advantages	Disadvantages
<p>Sonic Drilling: A high-power oscillator with eccentric weights driven by hydraulic motors drive a rotating and vibrating drill bit or core barrel into the ground</p>	<ul style="list-style-type: none"> Collection of continuous, relatively undisturbed unconsolidated and bedrock cores possible Higher drilling rates than conventional methods (around twice as fast as air rotary and 8 to 10 times faster than hollow-stem auger and cable tool) Produces about one tenth the cuttings of hollow-stem auger and cable tool 	<ul style="list-style-type: none"> Higher operation, maintenance, and tooling costs compared to conventional drilling methods Present equipment limited to depths of about 300 ft Drilling in hard rock generally not recommended Driving of material into borehole wall might create problems for borehole logging and aquifer testing Limited equipment availability
<p>Directional Drilling: Various types of rigs capable of drilling slanting or horizontal holes; common features include a steerable drill stem and devices for detecting drill head location or trajectory</p>	<ul style="list-style-type: none"> Allows borehole access to subsurface areas such as beneath buildings, tanks, landfills, and impoundments where vertical drill rigs cannot go Reduces potential for cross-contamination between aquifers Excellent for remediation techniques that require maximum horizontal access to contaminated zone or contaminant plumes that are not vertically dispersed Production from horizontal wells generally is higher than that from vertical wells due to greater possible screen length 	<ul style="list-style-type: none"> There has been relatively little actual experience using directional drilling methods at contaminated sites, and value for site characterization and monitoring (as opposed to remediation) has yet to be demonstrated Drilling costs are high for petroleum industry-related equipment (\$100 to several hundred dollars a foot) Utility rigs, although less expensive than petroleum rigs, have more limited depth capabilities (around 20 ft compared to 300 ft for EC slant rig) Equipment that uses water or other fluids to advance the well bore might affect quality of samples Sampling capabilities are currently limited
<p>Cable Tool (Percussion): Hole created by dropping a heavy "string" of drill tools into well bore, crushing materials at bottom; cuttings are removed periodically by bailer; generally, casing is driven just ahead of the bottom of the hole, which is typically greater than 6 in. in diameter</p>	<ul style="list-style-type: none"> Can be used in rock formations as well as unconsolidated formations Fairly accurate logs can be prepared from cuttings if collected frequently enough Driving a casing ahead of hole minimizes cross-contamination by vertical leakage of formation waters Core samples can be obtained easily 	<ul style="list-style-type: none"> Requires an experienced driller Heavy steel drive pipe used to keep hole open and drilling tools can limit accessibility Cannot run some geophysical logs due to presence of drive pipe Relatively slow drilling method
<p>Jetting: Washing action of water forced out of the bottom of the drill rod clears hole to allow penetration; cuttings brought to surface by water flowing up the outside of the drill rod</p>	<ul style="list-style-type: none"> Inexpensive; driller often not needed for shallow holes In firm, noncavey deposits where hole will stand open, well construction fairly simple 	<ul style="list-style-type: none"> Somewhat slow, especially with increasing depth Extremely difficult to use in very coarse materials, i.e., cobbles/boulders A water supply is needed that is under enough pressure to penetrate the geologic materials present Difficult to interpret sequence of geologic materials from cuttings Maximum depth of 150 ft, depending on geology and water pressure capabilities
<p>Jet Percussion: Similar to jetting except a wedge-shaped drill bit is attached to a cable that is alternately raised and dropped</p>		
<p>Diamond Rotary: Rotating bit consists of a tube 10 to 20 ft long with a diamond-studded ring fitted to the bottom; diamond bit cuts through rock, with solid core of rock remaining in tube</p>	<ul style="list-style-type: none"> Takes continuous rock sample for accurate geologic logging Can be used with hydraulic or air rotary drill rig 	<ul style="list-style-type: none"> Expensive; diamond bits are more expensive than conventional roller bits If used with hydraulic rotary, drilling muds may contaminate well Slow compared to most other methods

Source: Adapted from U.S. EPA (1987a) and Boulding (1993b).

Table 9.4 Advantages and Disadvantages of Monitoring Well Casing Materials

Method	Advantages	Disadvantages
Plastic casing	<ul style="list-style-type: none"> • Lightweight • PVC is inexpensive • Generally good to excellent chemical resistance; fluoropolymers have the best chemical resistance, except for fluorinated solvents; PVC has poor resistance to high concentrations of aromatic hydrocarbons (toluene, xylene, trichlorethylene), esters, and ketones 	<ul style="list-style-type: none"> • Weaker, less rigid, and more temperature sensitive than metallic materials (PTFE/TFE is especially low, PVDF is stronger; ABS has low strength and less heat resistance than PVC) • PVC might adsorb some constituents from ground water • PVC might react with and leach some constituents into ground water, and PTFE is prone to sorption of selected organic compounds (proper purging and sampling procedures can minimize these problems) • Fluoropolymers are expensive (PVDF is less expensive than PTFE/TFE) • Some materials are not commonly available (ABS, PVDF) • Tensile strength of wear resistance of PTFE/TFE is low compared to other plastics, and screen slot opening might decrease in size over time • Antistick properties of fluoropolymer materials make it difficult to achieve an annular seal with neat cement grout, creating potential for alteration of ground-water chemistry by percolating surface water
Metallic	<ul style="list-style-type: none"> • Stainless steel has least adsorption of halogenated and aromatic hydrocarbons • All steel casings have high strength and generally are not temperature sensitive • Stainless steel has excellent resistance to corrosion and oxidation • Stainless steel is readily available in all diameters and screen slot sizes • Mild steel is readily available and less expensive than stainless steel for casing 	<ul style="list-style-type: none"> • Heavier than plastics • Stainless steel might corrode and leach some chromium in highly acidic water and might act as a catalyst in some organic reactions • Stainless steel screens are more expensive than plastic screens • Mild steel might react with and leach some constituents into ground water and is not as chemically resistant as stainless steel • Under saturated conditions carbon and low carbon steel rust easily, providing a highly sorptive surface for many metals, and they deteriorate in corrosive environments • Zinc might leach from galvanized steel, and if the coating is scratched, will rust, providing a highly sorptive surface for metals
Fiberglass reinforced	<ul style="list-style-type: none"> • High strength (almost as strong as stainless steel) • Light (weighs about the same as PVC) • Limited available data indicate that it is relatively inert in most monitoring well environments 	<ul style="list-style-type: none"> • Some adsorption of volatile organics (can be overcome by proper purging and sampling procedures) • Not readily available and little data available on its performance in the field

Source: Adapted from Boulding (1993b).

slot screen (V-shaped continuous wire is wrapped around vertical rods). [Figure 9.3](#) illustrates these two well screen types.

9.3.2 Filter Pack, Grouts, and Seals

The filter pack, also called a *gravel* or *sand* pack, is usually placed around a well screen to (1) increase hydraulic conductivity around the well screen, and (2) keep fine particles from entering the well screen during ground-water sampling. Desirable *artificial* filter pack characteristics include:

- Uniform grain size to minimize loss of material during development and development time
- Well-rounded grains to increase hydraulic conductivity, porosity, yield, and effectiveness of well development

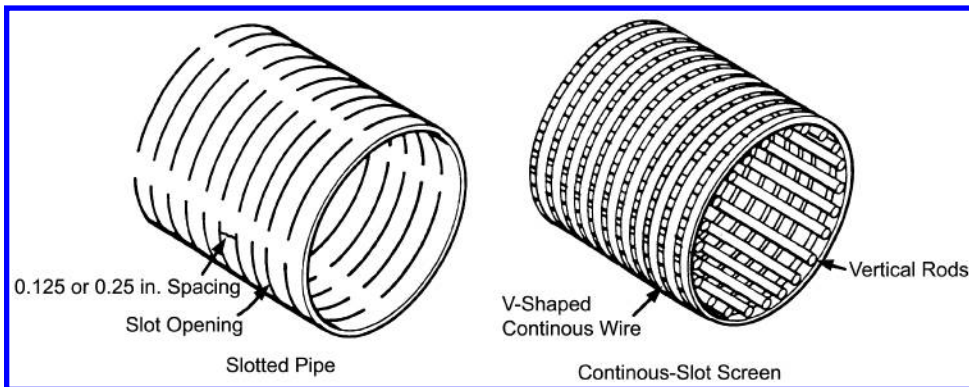


Figure 9.3 Commonly used monitoring well screen types (Boulding, 1993b, after Nielsen and Schalla, 1991).

- Ninety to 95% quartz grains to minimize changes to ground-water chemistry and to eliminate loss of volume by dissolution of minerals
- Uniformity coefficient of 2.5 or less to minimize separation during installation and lower head loss

Alternatively, when *natural filter pack* is used, well screen slot size is determined based on the particle-size distribution in the aquifer materials and the fines are removed during the development process. Table 9.5 summarizes the relative advantages and disadvantages of artificial and natural filter packs.

In relatively shallow wells, the filter pack can be placed by simply dumping sand down the annulus (provided the annular space is more than 2 in.). More typically, the filter pack is placed by pouring the sand into a *tremie pipe*, a rigid or partially flexible tube of pipe that allows funneling of the material directly to the interval around the well screen. Other methods of emplacement include the *reverse circulation method*, where a sand and water mixture is fed into the annulus around the well screen and the water entering the screen is pumped up to the surface, and *backwashing*, where water is pumped down the well and allowed to rise up around the annular area as filter pack material filters down through the rising water.

Grouts are used in monitoring well constructions to seal the annular space between the well casing and the formation to prevent contaminants from moving upward or downward to uncontaminated areas. The two major types of grouts are (1) bentonite and (2) neat cement. *Bentonite* can be placed either as unhydrated pellets or chips with water added later or pumped down through a tremie pipe as a slurry. *Neat cement* (a mixture of 5 to 6 gal of clean water per 1 ft³ bag of Portland cement, usually Type I) is mixed manually or with a mechanical mixture and pumped into the annulus. Table 9.5 also summarizes the relative advantages and disadvantages of bentonite and cement grouts.

A variety of additives can be mixed with the cement slurry to change the properties of the cement. The more common *cement additives* include:

- *Bentonite*, which improves workability and reduces weight and shrinkage
- *Calcium chloride*, which accelerates setting time and creates higher early strength (especially useful in cold climates)
- *Gypsum*, which creates a quick-setting (but expensive) expanding cement
- *Aluminum powder*, which produces a strong, quick-setting cement that expands on setting
- *Fly ash*, which increases sulfate resistance and early compressive strength
- *Hydroxylated carboxylic acid*, which retards setting time and improves workability without compromising set strength
- *Diatomaceous earth*, which reduces slurry density and thickening time, but increases water demand and reduces set strength

Table 9.5 Advantages and Disadvantages of Filter Pack, Grouts, and Seals

Method	Advantages	Disadvantages
Artificial filter pack	Characteristics of the filter pack material can be selected for optimum efficiency of well operation	<ul style="list-style-type: none">• Procedure is relatively time-consuming and expensive• Bridging might prevent complete filling around the well screen• Extension of filter pack above or below the screen area might allow contaminants to move to uncontaminated areas• Filter pack material might introduce contaminants into the aquifer (a leaching test can be used to determine whether this might be a problem)• Use of reverse circulation and backwashing emplacement methods might alter ground-water chemistry
Natural filter pack	<ul style="list-style-type: none">• Simpler and can be less expensive (depending on time requirements for well development)• Potential for alteration of ground-water chemistry is minimized	<ul style="list-style-type: none">• Well development is more difficult, and success is less assured• Selection of optimum screen slot size is more difficult
Bentonite grout	<ul style="list-style-type: none">• Readily available• Inexpensive• Pellets or slurry can be used	<ul style="list-style-type: none">• Possible constituent interference due to ion exchange• Complete seal and complete bond to casing not assured• Pellets can bridge or wet and swell, sticking to the formation or casing before filling the annular space• Can clog pump if slurry gets too dense
Cement grout	<ul style="list-style-type: none">• Readily available• Inexpensive• Can use sand or gravel filler• Possible to determine how well the cement has been placed by means of temperature or sonic bond logs	<ul style="list-style-type: none">• Chemical interferences (high pH with attendant change in ground-water chemistry)• Mixer, pump, and tremie lines are required, and more cleanup generally is required than with bentonite• Possible problems getting the material to set up• Channeling between the casing and seal can develop because of temperature changes during the curing process, swelling and shrinkage of the grout while the mixture cures, and poor bonding between the grout and the casing surface• Heat from setting can compromise structural integrity of some well casing materials (i.e., thermoplastic)

Source: Adapted from Boulding (1993b).

Cement and additives have the potential for affecting ground-water quality (especially pH and iron; see Table 5.9). This is most likely to be a problem if a poor annular seal is achieved (Figure 9.4), but any special additives should be carefully evaluated for the potential effects on ground-water chemistry.

Major *surface sealing* measures include (1) placement of a sturdy protective outer casing with cover and lock to a depth below the frost line and a drainage hole to prevent moisture buildup between the protective casing and the well casing, and (2) placement of a concrete pad sloping away from the casing to prevent infiltration of surface water and shaped so as to prevent frost heaving. Figure 9.4 illustrates the types of potential pathways for fluid movement when the borehole annulus is incorrectly grouted and sealed.

9.3.3 Well Development

After grouting and sealing are completed, *well development* is essential to remove fines from the filter pack around the well screen in order to improve hydraulic performance and eliminate or reduce collection of sediment in water quality samples. Well development is also necessary to

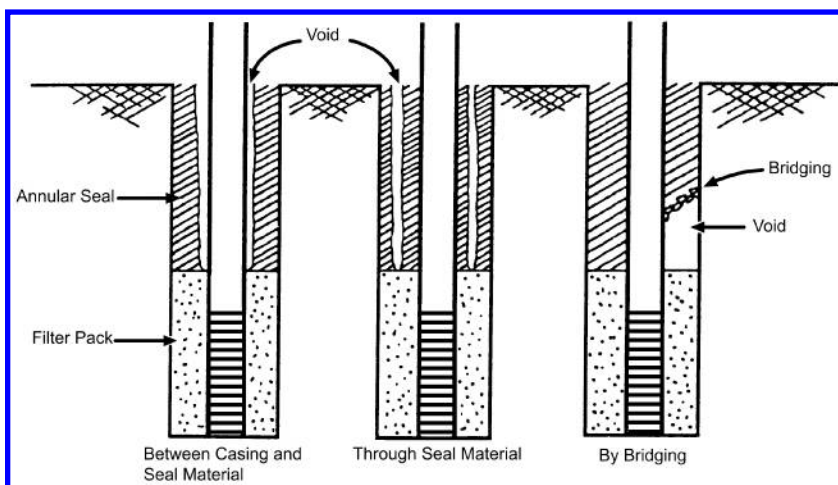


Figure 9.4 Potential pathways for fluid movement in the casing-borehole annulus (Boulding, 1993b, after Aller et al., 1991).

rectify damage done during drilling to borehole wall and adjacent formation, as occurs when drilling muds are used.

A variety of techniques are used to develop wells. In *overpumping*, the well is pumped at a rate that substantially exceeds the ability of the formation to deliver water. *Backwashing* often is used in conjunction with overpumping. If the pump does not have a backflow prevention valve, alternately starting and stopping the pump creates a surging effect where water is driven back into the formation during the off cycle. Alternatively, water can be added to the well. In *bailing*, a bailer (Section 9.5.2) is allowed to fall freely through the borehole until it strikes the surface of the water. The impact of the bailer produces an outward surge of water through the well screen and filter pack. As the bailer fills, the flow of water reverses and fines migrate into the well and are brought to the surface in the bailer. Sediment in the bottom of the well can be mobilized by short rapid strokes of the bailer near the bottom before retrieving the bailer.

Mechanical surging forces water into and out of the well screen by operating a plunger, called a *surge block*, which is attached to a drill rod or a wire line. The surge block is lowered to the top of the well intake and operated in a pumping action with strokes typically around 3 ft and is gradually worked downward through the screened interval. At regular intervals, the surge block is removed and fines that have entered the well are removed by pumping or with a bailer. *Compressed air* can be used to alternately surge and air-lift pump a well to remove sediment. In *air surging*, injected air lifts the water column until it reaches the top of the casing and the air supply is shut off, causing an outward surging action in the well intake. *Air-lift* pumping uses compressed air to bring water to the surface. *High-velocity jetting* uses a single- or multiple-nozzle device that directs a horizontal stream of water against the well screen opening. The jetting tool is placed near the bottom of the screen and slowly rotated while being pulled upward. Material that enters the screen in the backwash of the jet stream is removed by pumping or bailing. *Jetting/pumping*, which combines jetting with simultaneous pumping, provides for maximum development efficiency. Two development methods that are used for water wells but are not recommended for monitoring well development because they introduce contaminants into the aquifer are (1) *blasting* (used only in solid rock wells) and (2) *acidizing* (used only in limestone aquifers).

Overpumping and backwashing are probably the most commonly used forms of well development. These methods or bailing combined with mechanical surging will be the most effective methods for most situations. Table 9.6 summarizes relative advantages and disadvantages of the main methods described previously.

Table 9.6 Advantages and Disadvantages of Well Development Methods

Method	Advantages	Disadvantages
Overpumping	<ul style="list-style-type: none">• Convenient for small wells or poor aquifers• Minimal time and effort are required• No new fluids introduced• Removes fluids introduced during drilling and fine sediments	<ul style="list-style-type: none">• Not adequate for large wells• Will not develop maximum efficiency in a well because does not effectively remove fine-grained sediment• Tends to cause sand to bridge in the formations (can be reduced by alternating pump on and pump off)• Requires the use of high capacity pumping equipment• Can result in a large volume of water to be contained and disposed• Can leave the lower portion of large screen intervals undeveloped• Excessive pumping rates can cause well collapse, especially in deep wells• Equipment for effective overpumping might not fit in small-diameter wells
Backwashing	<ul style="list-style-type: none">• Effectively rearranges filter pack• Effective in breaking down bridging• No new fluids introduced with on-off overpumping	<ul style="list-style-type: none">• Fine sand, mud, silt, or clay can be washed into the well or filter pack from the formation• Not fully effective unless combined with surging, bailing, or pumping• Large quantities of water are required• Unless combined with pumping or bailing, does not remove drilling fluids• Backwashing with added water introduces fluid into the well that might alter formation chemistry
Bailing	<ul style="list-style-type: none">• No new fluids introduced into the aquifer• Removes fluids introduced during drilling• Removes fines from well• Bailers are easily obtained and can double as sampling devices	<ul style="list-style-type: none">• Time-consuming and tiring if done manually• Not as effective as surge blocks• Not effective in unproductive wells
Mechanical surging	<ul style="list-style-type: none">• Low cost• Effectively rearranges filter pack• Greater suction action and surging than backwashing• Breaks down bridging in filter pack• No new fluids are introduced• Convenient to use for cable tool rigs	<ul style="list-style-type: none">• Can produce unsatisfactory results when an aquifer contains clay because the casing or screen can collapse if it becomes plugged with fines• Tends to push fine-grained sediments into the filter pack• Unless combined with pumping or bailing, does not remove drilling fluids• Sometimes the well seal can be disturbed when surging• Excessive sand can result in sand-locking of the surge block
Compressed air	<ul style="list-style-type: none">• Rapid method	<p>Not recommended for monitoring wells because:</p> <ul style="list-style-type: none">• Air can become entrained in the filter pack and reduce permeability• Where yield is very weak and drawdown rapid, or submergence is low, other methods will be more satisfactory• Introduction of air into aquifer can alter chemistry
Jetting	<ul style="list-style-type: none">• Simple to use• Effectively rearranges and breaks down bridging in filter pack• Effectively removes mudcake around screen• Jetting with simultaneous pumping is particularly successful for wells in unconsolidated sands and gravels• Jetting/pumping removes sediment from the well before it can settle in the screen, and jetting waters can be recirculated after sediment has been removed at the surface	<p>Generally not recommended because:</p> <ul style="list-style-type: none">• Foreign water and possible contaminants are introduced to the aquifer• Air blockage can develop with air jetting• Air jetting can change water chemistry and biology (iron bacteria) near well• Unless combined with pumping or bailing, does not remove drilling fluids• Jetting with simultaneous pumping is not always practicable

Source: Adapted from Boulding (1993b).

9.3.4 Well Maintenance, Rehabilitation, and Abandonment

Well *maintenance* involves the routine, ongoing tasks that ensure a well is a representative sampling point. This involves full documentation of design and installation of the well and of all subsequent sampling and other activities involving the well.

Routine well maintenance activities include:

- Periodic bail testing of the well to determine specific capacity (can be done during normal purging for sampling or more frequently if sampling is infrequent)
- Measurement of depth before purging
- Repair of protective casing, covers, hinges, and any other exposed parts of the well
- Occasional redevelopment by bailing, surging, or bottom pumping

Rehabilitation involves efforts beyond normal maintenance that are intended to restore the well's original performance or to alter the well to serve other purposes. Common rehabilitation techniques include (1) deepening because the water table has been lowered, (2) installation of sleeving to repair a physical problem, (3) treatment of screens to reduce plugging or encrustation, and (4) use of aggressive development techniques, such as high-velocity jetting (Section 9.3.3), to improve well performance. In traditional well rehabilitation, three categories of chemicals are used for rehabilitation: (1) *acids*, to dissolve incrustation on the well intake or in the surrounding formation; (2) *biocides*, to kill bacteria in the well or surrounding formation that contribute to clogging; and (3) *surfactants*, to disperse clay and fine materials for easier removal. Chemical treatment of monitoring wells is done only if the integrity of future sample collection can be assured.

Well *abandonment* or *decommissioning* involves the combination of full or partial casing/screen removal and plugging. The two main *casing/screen removal* techniques are (1) *pulling*, using hydraulic jacks or by pumping the casing with a rig, and (2) *overdrilling*, in which a large-diameter hollow-stem auger is used to drill around the casing. In shallow, sandy aquifers, casing can be removed by *jetting* (Section 9.2.3). *Sandlocking* can be used to remove telescoped well screens, where the diameter is smaller than the casing. A pulling pipe wrapped with burlap strips is lowered to penetrate about two thirds of the length of the screen. Sand is added to create a locking effect and the screen is pulled to the surface. *Latch-type* tools can be used to remove telescoped well screens that are 2 to 6 in. in diameter. *Partial casing removal* involves cutting the casing off below ground level.

The simplest technique for *plugging* an uncased borehole is to fill the entire hole with grout material, commonly a cement–bentonite mixture (Section 9.3.2), which is chemically compatible with the formation. Where casing is left in place, the interval adjacent to water-bearing zones is ripped or perforated with *casing rippers*, *gun perforators*, or *jet perforators*, and grouted under pressure to allow penetration outside the casing. *Partial grouting* requires the use of *bridge plugs*, which allow sealing of selected portions of a borehole. A *permanent bridge seal* is the most deeply located plug that forms a bridge upon which fill material can be placed and is used to prevent cross-contamination between lower and upper aquifers. If more than two water-bearing zones are intersected by the wells, *intermediate seals* are placed adjacent to intermediate zones and the remaining permeable zones are filled with clean disinfected sand, gravel, or other material. *Upper-most aquifer seals* keep out surface water and keep artesian aquifers from flowing to the surface. In artesian aquifers, special procedures might be required for plugging, such as (1) pumping nearby wells to lower hydrostatic head, (2) placing fluids of high specific gravity in the borehole, or (3) elevating the casing high enough to stop the flow. ASTM D5299 (Table A.14) provides more detailed guidance on well decommissioning.

9.3.5 Common Design Flaws and Installation Problems

Nielsen and Schalla (1991/T9.10) have identified six common monitoring well design flaws and installation problems that should be avoided.

1. Use of *well casing* or *well screen materials* that are not compatible with the hydrogeologic environment, known or suspected contaminants, or the requirements of the ground-water sampling program. The result is chemical alteration of samples or failure of the well.
2. Incorrect *screen slot-sizing* practices or use of nonstandard types of well screen, such as field-slotted, drilled, or perforated casing. The result is well sedimentation and turbid samples throughout the monitoring program.
3. Improper *length* and *placement* of *well screens* so that discrete zones of the aquifer are missed or cannot be differentiated. In this situation, water level measurements and water quality samples might provide misleading results.
4. Improper selection and placement of *filter pack* materials. Consequences can include well sedimentation, well screen plugging, ground-water sample alteration, or potential well failure.
5. Improper selection and placement of *annular seal* materials. The results can include alteration of chemistry of water samples, plugging of the filter pack and well screen, and cross-contamination between water-bearing units that have not been adequately isolated.
6. Inadequate *surface protection measures*, such as surface seals that are susceptible to frost heave. The results can include surface water entering the well, chemical alteration of water quality samples, and well damage to destruction.

Another common installation problem that can be added to this list occurs after installation has been completed.

7. Use of improper *well development* techniques. The results can include continuing turbidity in water quality samples due to failure to remove fines for the well screen and filter pack, chemical alteration of water quality samples due to the introduction of air or foreign water into the aquifer, and possible damage to the well screen by stresses caused by excessive surging.

9.4 SAMPLING SUBSURFACE SOLIDS AND THE VADOSE ZONE

This sections covers four distinct, but interrelated types of subsurface sampling: (1) soil and geologic materials above and below the saturated zone, (2) soil gas sampling in the vadose zone, (3) soil-solute sampling in the vadose zone, and (4) microbiological sampling.

9.4.1 Subsurface Solids Sampling

Solids sampling methods can be broadly classified as (1) handheld and (2) power driven. Criteria for selection of *handheld* equipment includes (1) whether an undisturbed core is required, (2) soil conditions at the site (cohesion, stones, moisture), (3) the sample size and depth desired, and (4) the number of required operators. Many specific types of handheld sampling devices are available. Table A.9 provides information on applications and limitations of 20 types in the following categories: (1) grab samplers (spoons, scoops, shovels, and picks), (2) augers, and (3) tube samplers. Handheld soil samplers are usually used for sampling the near surface (2 to 3 m). *Grab* samplers are commonly used for near-surface sampling for initial screening purposes. *Augers* are typically used for collection of composite near-surface samples and in combination with tube samplers to collect undisturbed samples at different depths. *Tube* samplers are used for observation of subsurface soil characteristics and collection of undisturbed cores for laboratory study. Both augers and tube samplers require the use of *liners* when sampling for volatile contaminants in order to minimize contact of samples with the atmosphere.

Power-driven samplers are usually operated in conjunction with drill rigs, cone penetration rigs, or hydraulic devices attached to smaller trucks. Portable power-driven augers that can be used by one or two persons are also available. Table A.10 provides information on applications and limitations on 18 specific power-driven sampling devices in the following general categories: (1) disturbed core samplers and (2) undisturbed core samplers. *Disturbed core* samplers include various

types of *barrel* samplers and *rotating core* samplers. *Undisturbed core* samplers might better be called *minimally disturbed* core samplers, since some disturbance is inevitable. These samplers fall into three major categories: (1) *thin-wall open tube* (including the *Shelby tube* and *Laskey continuous sampler*); (2) *thin-wall piston* samplers, which are especially useful for collecting sample on noncohesive materials; and (3) samplers for other specialized situations, such as hard, dense, brittle, and cohesive soils.

Collection of soil cores is the preferred method for sampling solids because much more accurate lithologic logging is possible than with cuttings from drill methods that do not obtain cores as part of the drilling process, such as diamond drilling (Section 9.2.3). The most common method for collection of disturbed cores is the *split-spoon* sampler, also called a *split-barrel* sampler. Thin-wall open-tube samples are the most common method for collecting undisturbed cores in unconsolidated materials. As noted above, thin-wall piston samplers are usually used where poor cohesion prevents good recovery with conventional thin-wall samplers, and specially designed thin-wall samplers are required for gravelly and very stiff or cemented unconsolidated deposits. Murphy and Herkelrath (1996)⁶ describe modifications to a wire line piston core sampler that allow freezing of the lowest 3 in. for recovery of full cores in saturated and nearly saturated sands.

ASTM D4700 provides general guidance on selection of soil sampling devices and sample collection in the vadose zone, and ASTM D6169 provides guidance on selection of soil and rock sampling devices used with drill rigs (Table A.14). ASTM guides for specific sampling devices include D1452 (augers), D2113 (diamond core drilling), D3350 (ring-lined barrel), D1586 (split barrel), and D1587 (thin-wall tube).

9.4.2 Soil Gas Sampling

Sampling of soil gas above the zone of saturation and analyzing for the presence of volatile organic compounds (VOCs) is a relatively new technique in contaminant hydrogeology that began in the early 1980s and has gained rapid acceptance. A variety of sampling techniques are used for soil gas survey. *Passive* sampling uses an *in situ* adsorbent (usually an activated charcoal rod), which is buried in the soil for a few days to weeks. The adsorbent is then retrieved and analyzed for VOCs in a laboratory by mass spectrometry or gas chromatography. *Dynamic* or *grab* sampling involves the installation of a probe or soil boring in the vadose zone, followed by withdrawal of soil gas by a pump. Soil gas samples taken with this method can be analyzed on-site using portable gas chromatographs (Section 9.6.2). The most common uses of soil gas data are in planning monitoring well networks and defining the boundaries of contaminant plumes (Marrin and Kerfoot, 1988/T9.10).

Table 9.7 summarizes information on seven major groups of organic contaminants relevant to soil gas surveying. Contaminants in Group A (halogenated methanes, ethanes, and ethenes) and Group D (lighter petroleum hydrocarbons) are the most likely candidates for this method, followed by Group G (low-molecular-weight oxygenated compounds) if the leak or spill is in dry soil.

Soil gas measurements taken areally at the same depth allow creation of an isopleth map that might look something like the resistivity measurements in Figure 6.6. Sampling at different depths at a single point and plotting concentration against depth allows some inferences about subsurface conditions. Figure 9.5 shows VOC concentration profiles with increasing depth in a variety of hydrogeologic settings. Figure 9.5a shows that in homogenous unsaturated porous media, VOC concentration is lowest at the surface and increases steadily to a maximum at the contaminant source. Impermeable layers cause different VOC concentration profiles, depending on where they are located (see Figure 9.5b and c). Microbiological activity may reduce VOC concentrations near the ground surface (see Figure 9.5d), and a VOC source in the vadose zone creates a profile where concentrations decline with distance in all directions from the source (see Figure 9.5e).

⁶ Murphy, F. and W.N. Herkelrath. 1996. A Sample-Freezing Drive Shoe for a Wire Line Piston Core Sampler. *Ground Water Monitoring and Remediation* 16(3):86–90.

Table 9.7 Characteristics of Contaminants in Relation to Soil Gas Surveying

Group/Contaminants	Applicability of Soil Gas Survey Techniques
Group A: Halogenated Methanes, Ethanes, and Ethenes	
Chloroform, vinyl chloride, carbon tetrachloride, trichlorofluoromethane, TCA, EDB, TCE	Detectable in soil gas over a wide range of environmental conditions; dense nonaqueous phase liquid (DNAPL) will sink in aquifer if present as pure liquid
Group B: Halogenated Propanes, Propenes, and Benzenes	
Chlorobenzene, trichlorobenzene, 1,2-dichloropropane	Limited value; detectable by soil gas techniques only where probes can sample near contaminated soil or ground water; DNAPL
Group C: Halogenated Polycyclic Aromatics	
Aldrin, DDT, chlordane, heptachlor, PCBs	Do not partition into the gas phase adequately to be detected in soil gas under normal circumstances; DNAPL
Group D: C₁ to C₈ Petroleum Hydrocarbons	
Benzene, toluene, xylene isomers, methane, ethane, cyclohexane, gasoline, JP-4	Most predictably detected in shallow aquifers or leaking underground storage tanks where probes can be driven near the source of contamination; light nonaqueous phase liquids (LNAPLs) float as thin film on the water table; can act as a solvent for DNAPLs, keeping them nearer the ground surface
Group E: C₉ to C₁₂ Petroleum Hydrocarbons	
Trimethylbenzene, naphthalene, decane, DNAPLs	Limited value; detectable by soil gas techniques only where probes can sample near contaminated soil or diesel and jet A fuel ground water
Group F: Polycyclic Aromatic Hydrocarbons	
Anthracene, benzopyrene, fluoranthene, chrysene, motor oils, coal tars	Do not partition adequately into the gas phase to be detected in soil gas under normal circumstances; DNAPLs
Group G: Low-Molecular-Weight Oxygenated Compounds	
Acetone, ethanol, formaldehyde, methylethylketone	LNAPLs, but dissolve readily in ground water; may be detected in soil gas if they result from a leak or spill in relatively dry soil

Source: Adapted from Marrin (1987).

9.4.3 Soil-Solute Sampling

Monitoring of soil water in the vadose zone can serve as an early warning system at controlled waste disposal sites that contaminants are entering the subsurface and can allow actions to be taken before contaminants reach the saturated zone. Methods for sampling and monitoring the vadose zone can be broadly categorized as (1) *indirect* (surface geophysical methods and probes that focus on measuring variations in soil salinity), and (2) *direct* (in which soil water is collected directly in the field or extracted from samples of soil solids).

Indirect Soil Salinity Measurements. A variety of methods are available for locating and monitoring areas of high soil salinity. These methods primarily have been developed for agricultural applications to identify saline soils and control irrigation flows where soluble salts can affect crop productivity. Table A.11 summarizes information on six indirect methods for monitoring soil salinity. The *four-probe electrical* method is a direct application of the electrical resistivity surface

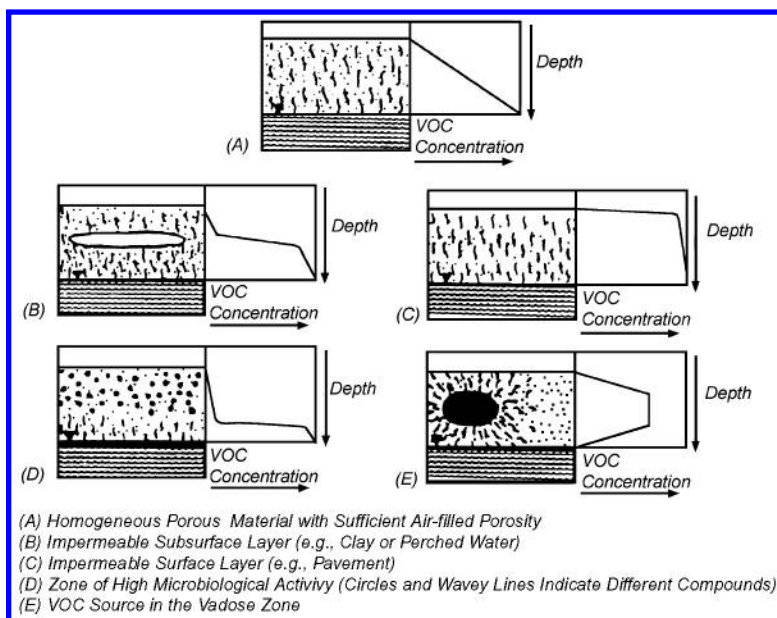


Figure 9.5 Soil gas concentrations under a variety of hydrogeologic conditions (Boulding and Barcelona, 1991c, after Marrin and Kerfoot, 1988).

geophysical method (Section 6.3.2), with electrode configurations that measure near-surface resistivity. The *electromagnetic induction sensor* is an instrument that is specifically designed to measure conductivity in the near surface. The other indirect methods involve placement of probes or sensors in the subsurface. The main advantage of indirect methods is that data can be collected quickly. The main disadvantages are that (1) instruments must be calibrated for each soil type by collection of samples where salinity is measured directly to obtain quantitative measurement of soil salinity; and (2) actual chemical constituents that are contributing to soil salinity cannot be determined. The four-probe electrical and porous matrix soil salinity sensors are the most commonly used indirect methods.

Direct Soil-Solute Sampling Methods. Three major types of soil water can be identified in the context of sampling soil water: (1) *macropore* or *gravitational* water, which flows through the soil relatively rapidly in response to gravity (excess of 0.1 to 0.2 bars suction); (2) *soil-pore* or *capillary* water, which is held in the soil at negative pressure potentials from around 0.1 to 31 bars of suction; and (3) *hygroscopic* water, which is held at tensions greater than 31 bars suction. Soil-pore water moves through the vadose zone, but at much slower rates than gravitational water (Section 2.4.1), whereas hygroscopic water, if it moves, does so primarily in the vapor form. The term *soil-solute* or *solution* sampling has been used loosely in the literature to describe most sampling methods, whereas the term *soil-pore liquid* is typically used in a more restricted sense (and is so used here) to apply to sampling of capillary water. The chemistry of soil-solute sampling methods can differ significantly, depending on the method used. Concentrations of inorganic species generally increase as the matric potential increases. In general, ceramic soil suction samplers (which use suctions up to around 0.8 bars) will collect samples that are most representative of the soil solution for the purpose of evaluating contaminant transport.

There are a large number of specific methods by which soil water can be sampled. *Suction* samplers draw water from the soil by applying a vacuum. A variety of *free-drainage* samples collect water percolating through the soil by gravity flow. *Capillary wick* samplers are a relatively new development, which appear to have good potential for collecting more representative samples of soil solutions than either porous cup or free-drainage samplers in the near surface. Other methods

include (1) use of absorbent materials with retrieval and extraction of water in the laboratory, (2) collection of soil solids with extraction of soil water in the laboratory by a variety of methods, and (3) preparation of a soil saturation extract from a solids sample. Table A.11 summarizes some information on six types of suction samplers, seven methods of collecting samples by free drainage, and four miscellaneous methods.

The main advantages of suction samplers are that they are relatively easy to install and there are essentially no limitations to the depth of sampling when a vacuum-pressure apparatus is used. The main disadvantage of suction samplers is that they might not collect representative samples. Sampling for organic chemicals, microorganisms, volatile chemicals, and metals is especially problematic due to potential sorption/interferences by the porous cup. Vacuum-type and vacuum-pressure-type porous cup samplers are by far the most commonly used types of suction samplers. The main advantage of free-drainage samplers is that a relatively large volume of water, which is representative of water that is actually percolating to deeper zones, is obtained. The main disadvantages are that installation procedures are time-consuming and complex and limited to relatively shallow depths. *Trench lysimeters* with pan collectors are the most commonly used free-drainage samplers. Figure 9.1 illustrates a variety of configurations for soil-solute sampling.

9.4.4 Microbiological Sampling and Other Sensitive Constituents

Special sampling procedures are required for sampling contaminants that can change in concentration (degassing of volatile compounds) or chemical composition (redox-sensitive chemical species, such as ferrous and ferric iron) when exposed to the air. Similar care is required when sampling for microbiota in the subsurface, especially where oxygen content is low (typically in the zone of saturation). Even where exposure to the air is not a concern for microbiological sampling (typically in the vadose zone), special care is required to make sure that the sample has not been cross-contaminated with soil microorganisms from higher soil horizons. The basic procedure involves collection of subsamples of power-driven sample cores (Section 9.4.1) using smaller-diameter corers.

Liners that fit inside a bucket auger or tube sampler are the best way to collect soil samples suspected of containing volatile organics. Alternatively, samples for volatiles should be quickly transferred to the sample container and sealed with no air headspace in the container. Where cores contain anaerobic bacteria and chemical species of concern that are in a reduced state, samples need to be extracted in an oxygen-free environment. Figure 9.6 shows a Plexiglas field glove box for collecting such samples. Sample containers are sterilized and filled with an inert gas such as nitrogen. In the field, the sealed containers are placed in the field glove box before the box is filled with nitrogen. The core sample is pushed into the box through an iris port, and a core paring tool is used to collect subsamples in the oxygen-free environment for placement in sample containers.

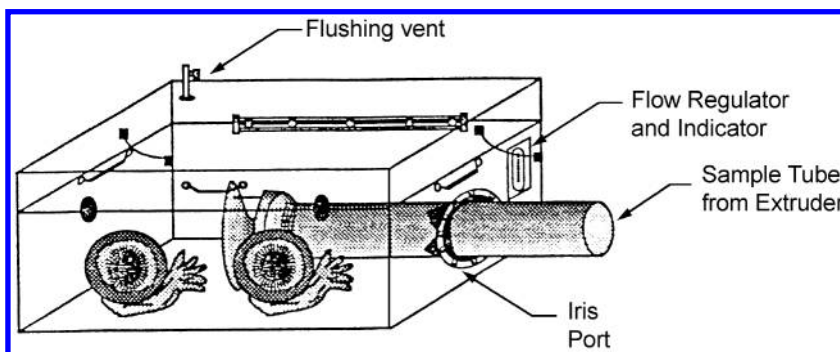


Figure 9.6 Field sampling glove box (Boulding, 1993b, after Leach et al., 1988).

9.5 SAMPLING GROUND WATER

A wide variety of devices and installations are available for the sampling of ground water. Sampling devices can be broadly classified as: (1) *portable well samplers*, which are used in permanently installed and screened monitoring wells, and (2) *in situ samplers*, which do not require cased monitoring wells. *In situ* sampling devices can be used for taking one-time samples or permanently installed in the subsurface as discussed in [Section 9.1.2](#). ASTM D5903 (Table A.14) provides guidance for planning and preparing for a ground water sampling event. Two recent ASTM guides address the issue of field filtration of ground water samples (D6564) and field preservation of ground water samples (D6517).

9.5.1 Portable Well Samplers

[Figure 9.7](#) shows a generalized flow diagram of the following major steps in collecting a sample from a monitoring well using a portable sampler: (1) well inspection, (2) purging (discussed in more detail in [Section 9.5.3](#)), (3) sample collection, (4) preservation and quality assurance/quality control (QA/QC) samples, and (5) storage and transport.

Table A.12 provides the following information on 20 portable sampling devices, which can be used to collect ground-water samples from wells: (1) maximum depth, (2) minimum well diameter, (3) typical ranges of sampling rates, and (4) sections and tables in the book where additional information can be found. Portable well samplers are divided into three main groups: (1) *positive displacement* samplers, (2) other sampling pumps, and (3) *grab-* and *depth-specific* samplers.

Positive displacement pumps are placed below the static water level of the well and pump the sample to the surface. These pumps include *bladder pumps* (also called *gas-operated squeeze pumps*), *gear-drive pumps*, *helical rotor pumps*, *gas-drive/displacement pumps* (where gas displaces water in the subsurface to force it to the surface without mixing with the sample), and *gas-drive piston* and *mechanical piston pumps*.

Other types of portable sampling pumps include *suction-lift* pumps (*peristaltic* pumps being the most common, but surface centrifugal and any other type of surface pump that operates using suction or a vacuum fall in this category), *submersible centrifugal pumps* (note that *surface* centrifugal pumps are classified as suction-lift pumps), *inertial-lift pumps* (simple mechanisms using foot valves and inertia to bring water to the surface), *gas-lift pumps* (where air or gas mixes with the water to bring ground water to the surface), and *jet* or *venturi* pumps. *Packer* pumps isolate a portion of the well using inflatable packers with the sample being brought to the surface using a suction-lift, submersible, or other sampling device.

The term *gas lift* (also sometimes called *air lift*) has been used inconsistently in the published literature on ground-water sampling devices. In this book the term refers to methods where gas mixes with water to provide the buoyant force to bring it to the surface, and *gas drive* refers to methods in which gas is used to push water up a tube without the gas becoming mixed with the water that is brought to the surface. For example, Morrison (1983/T9.10) and Scalf et al. (1981/T9.10) have used the term *lift* for samplers that are classified as gas-drive samplers in this guide.

Grab samplers include *bailers* (open and point-source), *mechanical* or *thief depth-specific* samplers (such as Kemmerer, Coliwas, stratified sample thief), and *pneumatic depth-specific* samplers, which use vacuum or pressure to activate the sampling mechanism (such as syringe and Westbay samplers).

Sampling devices vary greatly in their suitability for sampling different chemical constituents. [Table 9.8](#) summarizes the suitability of the 12 most commonly used sampling devices for 14 ground-water parameters. *Bladder* and *helical rotor* pumps are rated as suitable for the largest number of parameters, followed by *point-source bailers*. The *inertial pump*, which is not included in [Table 9.8](#), is a quite new device, which probably would rate favorably for sampling many of the parameters on the table.

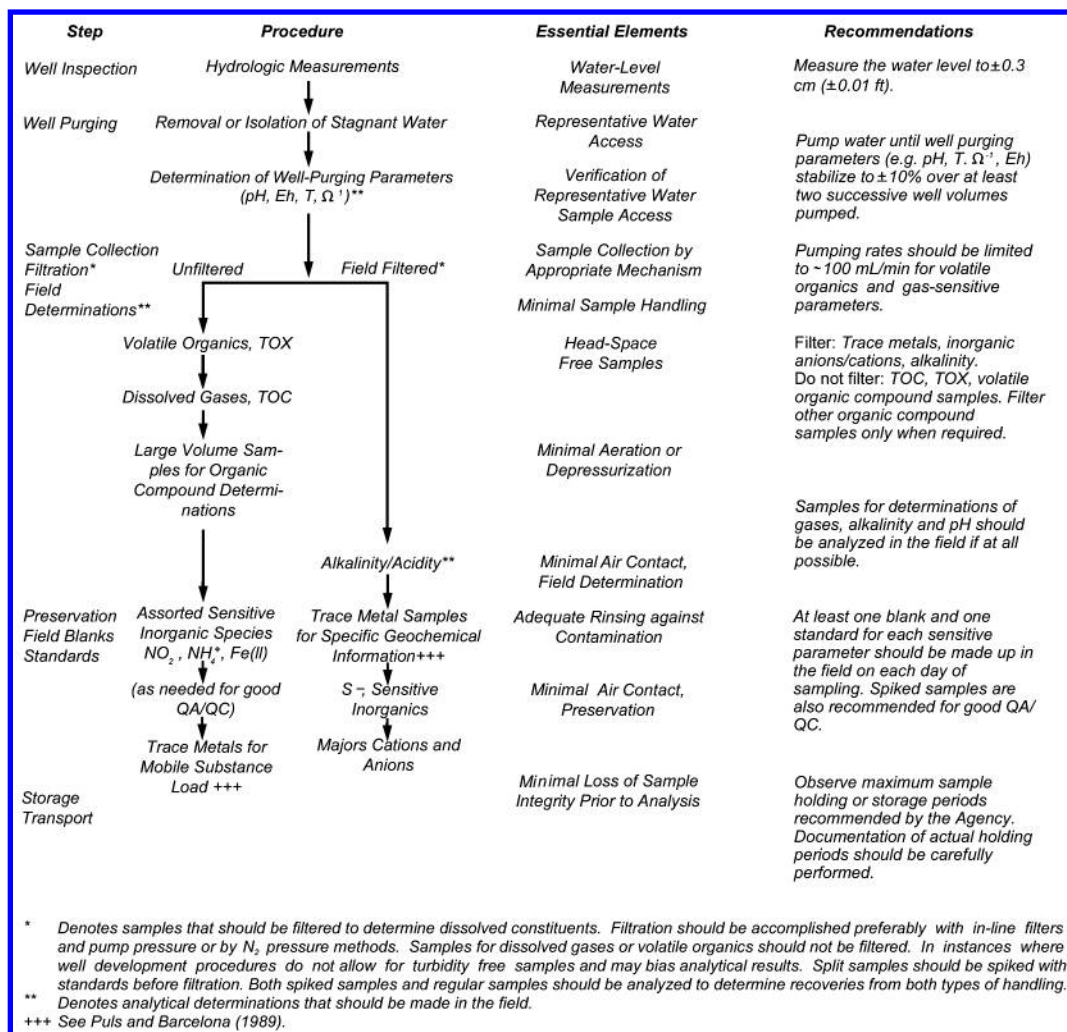


Figure 9.7 General flow diagram of ground-water sampling steps (Boulding and Barcelona, 1991c).

9.5.2 Portable/Permanent *In Situ* Samplers and Sensors

A relatively new development in ground-water sampling technology has been the design of *in situ* sampling probes, which can be used either for rapid collection of samples without the installation of permanent wells or left in place for continued monitoring. Table A.12 provides summary information on a variety of samplers and sensors of this type. The *Hydropunch*® and *BAT*® systems both operate in conjunction with conventional cone penetrometer rigs. This category also includes a variety of driven probes, which can be retrieved after sampling or left in place as permanent sampling points. Figure 9.2 illustrates several examples of permanent installations using the *BAT* system. These devices often are best used during the preliminary site characterization stage or where only a shallow water table is to be sampled. Portable *in situ* samplers can be valuable in deciding the best location of permanent monitoring wells. *Chemical sensors*, such as Eh and pH probes, and ion-selective electrodes usually are used in boreholes. Use of *fiber-optic*, *electrochemical*, *piezoelectric*, and other chemical sensors (see also Table A.13) for subsurface chemical characterization is the subject of considerable research and might become more widespread for routine investigations with further refinements in instrumentation. Strictly speaking, the term *in*

Table 9.8 Suitability of Major Ground Water Sampling Devices for Different Ground Water Parameters

Sampling Device	Inorganic							Organic				Other		
	EC	pH	Redox	Major Ions	Trace Metal	NO ₃ F	Dissolved Gases	Nonvolatile	Volatile	TOC	TOX	Radium	Alpha Beta	Coliform
Portable Grab/Depth-Specific Samplers														
Open bailer	x			x	x	x		x				x		x
Point-source bailer	x	x	x	x	x	x		x	x	x	x	x		x
Syringe sampler	x	x	x	x	x	x		x				x	x	x
Portable Positive Displacement (Submersible) Pumps														
Bladder	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Centrifugal	x			x		x						x	x	
Helical rotor	x	x	x	x	x	x	x	x	x	x	x	x	x	
Gas-drive piston	x			x	x	x		x				x	x	
Gear-drive									x					
Other Portable Samplers														
Peristaltic	x			x		x		x				x		x
Gas-drive/displacement		x			x		x		x				x	
Gas-Lift														
Portable <i>In Situ</i> Samplers														
Pneumatic	x	x	x	x	x	x		x				x	x	x

Note: TOC = total organic carbon; TOX = total organic halogen.

Source: Boulding and Barcelona (1991c), after Pohlmann and Hess (1988).

situ (from Latin, meaning in its original position) should only be applied to sampling devices or chemical sensors that measure ground-water quality in place without bringing the sample to the surface. In common usage, however, the term is applied to methods that allow collection of samples without the installation of a permanent monitoring well, or permanent installations that do not require use of portable sampling equipment.

9.5.3 Purging

Purging to remove stagnant water from a well before sample collection is standard practice. The monitoring well is pumped (generally at a rate of 1 to 5 gal/min) until a certain number of well volumes have been removed and until water quality indicators, such as pH, conductance, and temperature, have stabilized, indicating that fresh formation water fills the well. Sampling takes place after purging is completed. Recent research (Kearl et al., 1992)⁷ has suggested that purging is not desirable because it can mobilize colloidal particles upon which contaminants are sorbed. The alternative to purging is to use a dedicated sampling device set at the level of the well screen capable of low pumping rates (around 100 ml/min), which will not increase colloid density in the ground-water sample compared to natural colloidal flow through the well screen.

Recommended rules of thumb, such as purging three to five volumes (Fenn et al., 1977/T9.10), should be treated only as a starting point. Accurate estimation of purge volume requires knowing (1) well yield, determined from a slug or pumping test, and (2) the stagnant volumes of both the well casing and the sand pack. In slowly recovering wells, extra care is required when purging to ensure that water levels do not drop below the level of the well screen because aeration might allow loss of volatile or redox-sensitive contaminants. After stagnant water has been removed or isolated, chemical indicators (pH, conductance, and temperature) should continue to be monitored until they reach a consistent end point (no upward or downward trend). Flow-through cells with multiple probe ports (Garske and Schock, 1986)⁸ and multiple parameter probes are the most effective way to continuously monitor indicator parameters during purging.

Another important consideration in purging is that the pumping rate should not exceed levels that will cause turbulent flow. Turbulent flow in the well can cause pressure changes, which result in loss of carbon dioxide and other volatile gases, subsequently changing pH and dissolved solids content (Meredith and Brice, 1992).⁹ The maximum discharge rate during pumping that avoids turbulent flow is a function of hydraulic conductivity, the length of the well screen, width of the screen openings, and the total open area of the screen. Section B.2 in Boulding (1993/T9.10) includes a graph for determining the optimum screen entrance velocity related to the hydraulic conductivity of an aquifer and a table with guidelines for maximum purging rate based on screen type, diameter, slot size, open area, and entrance velocity.

Puls and Barcelona (1996)¹⁰ provide guidance on low-flow purging and sampling procedures that minimize the effects discussed above. More recently, ASTM has developed a guide for purging methods (ASTM D6452). When ground-water sampling is for regulatory purposes, the U.S. EPA or appropriate state regulatory agency should be consulted to determine appropriate procedures.

9.5.4 New Developments in Multilevel Sampling

Diffusion sampling of volatile organic contaminants ground water is an approach that avoids the concerns of ground water flow disturbance by purging and sampling noted in the previous

⁷ Kearl, P.M., N.E. Korte, and T.A. Cronk. 1992. Suggested Modifications to Ground Water Sampling Procedures Based on Observations from the Colloidal Boroscope. *Ground Water Monitoring Review* 12(2):155–161.

⁸ Garske, E.E. and M.R. Schock. 1986. An Inexpensive Flow-Through Cell and Measurement System for Monitoring Selected Chemical Parameters in Ground Water. *Ground Water Monitoring Review* 6(3):78–84.

⁹ Meredith, D.V. and D.A. Brice. 1992. Limitations on the Collection of Representative Samples from Small Diameter Monitoring Wells. *Ground Water Management* 11:429–439. [6th NOAC]

¹⁰ Puls, R.W. and M.J. Barcelona. 1996. Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures. *Ground Water Issue*, EPA/540/S-95/504, 12 pp.

section. Polyethylene bags filled with deionized water are lowered into a monitoring well screen interval and left in place for a sufficient length of time to allow concentrations of the contaminants in ground water to equilibrate with the water in the bags by diffusion. After an appropriate length of time (several weeks or more), the polyethylene bags are retrieved and the water is gently poured in sampling vials for analysis. The approach is inexpensive, requiring only sealable sandwich bags that can be purchased from a grocery store, and can be easily adapted to sampling multiple levels within a well.¹¹

Jones et al. (1999)¹² describe an inexpensive multiport polyethylene sock sampler that can be lowered into an open, uncased borehole. Each inlet port has its own tubing running to the surface. Depths of less than 30 ft can be sampled from the surface. For deeper sampling, each port feeds into a dedicated gas-drive or bladder pump. A 6-in. borehole can accommodate 10 sampling ports with pumps. Once installed, the sock is filled with bentonite slurry to push the sock and sampling ports against the borehole wall. The system has been used to depths of 150 ft in a sandstone aquifer.

9.6 FIELD SCREENING AND ANALYTICAL METHODS

The term *field screening* has gained widespread use in recent years to describe a wide variety of methods for chemical characterization of contaminated sites. In this book, a distinction is made between field screening and field analytical methods. *Field screening* methods provide an indication of the presence or absence of a particular chemical or chemical class of concern or provide an indication of whether the chemical or chemical class of concern is above or below a predetermined threshold. Screening methods provide relative concentrations for chemical classes, but rarely provide chemical-specific information. This definition is more restrictive than those usually found in the literature. *Field analytical* methods include all chemical analysis methods capable of providing chemical-specific quantitative data in the field or nonlaboratory setting. Field analytical techniques generally are more rapid and less expensive than similar chemical analyses performed in laboratories with fixed facilities. Field screening and analytical techniques can be classified as *portable* (require no external power source, are compact, and are rugged enough to be carried by hand into the field), *fieldable* (require limited external power, are compact, and are rugged enough to be transported in a small van, pickup, or four-wheel drive), or *mobile* (are small enough to carry in a mobile laboratory, which is feasible for most analytical instruments, although power considerations can be a limitation). The standards by which the sensitivity, precision, and accuracy of field screening techniques are measured are those obtained in fixed-base laboratories in EPA's *Contract Laboratory Program* (CLP). An intermediate option for analysis of samples is the use of a *dedicated* laboratory using CLP procedures but involving more rapid turnaround time (as short as overnight) for sample results.

9.6.1 Field Analysis vs. CLP Analytical Laboratory

Key advantages of field analytical techniques include the following: (1) results can be obtained within hours, compared to the 20 to 40 days required for CLP laboratories, which allows for more rapid definition of the scope of contamination and allows for optimal selection of permanent monitoring wells and locations; (2) lower cost per sample (commonly one tenth the CLP cost) allows for more detailed characterization of contaminant distribution and reduced overall costs; and (3) the techniques are best suited for preliminary site characterization, emergency remedial actions, and monitoring of remediation activities. Some general disadvantages of field analytical techniques include the following: (1) application of analytical QA/QC procedures is more difficult

¹¹ Vroblesky, D.A. and W.T. Hyde. 1997. Diffusion Samplers as an Inexpensive Approach to Monitoring VOCs in Ground Water. *Ground Water Monitoring and Remediation* 17(3):177–184.

¹² Jones, I., D.N. Lerner, and O.P. Baines. 1999. Multiport Sock Samplers: A Low-Cost Technology for Effective Multilevel Ground Water Sampling. *Ground Water Monitoring and Remediation* 19(1):134–142.

in the field; (2) generally, less sophisticated instrumentation and disadvantage number 1 result in generally higher detection limits and lower precision and accuracy compared to CLP laboratories; and (3) disadvantages numbers 1 and 2 mean that data are more liable to challenge by litigation.

Cost differences between field analysis and laboratory analysis are strongly dependent on the number of samples from a site that must be analyzed, with the cost advantage tending to shift to field analysis as the number of samples increases. For example, if less than 30 to 50 cumulative samples are required, laboratory gas chromatograph analyses are likely to be less expensive than using portable or mobile gas chromatographs. Similarly, around 50 to 80 cumulative samples for field x-ray fluorescence analysis of metals are required to save money over conventional laboratory x-ray fluorescence (XRF) analyses.

9.6.2 Overview of Specific Techniques

Developments in miniaturization and computer processing of analytical signals and development of innovative analytical techniques mean that almost any instrumental or analytical technique has the potential for being used for field screening. Any attempt to publish a comprehensive compilation of techniques that have been proposed or tested is doomed to be out-of-date before it reaches print. Table A.13 provides summary information on over 80 techniques. This table provides a reasonably comprehensive overview of the state of the art as of early 1993. Techniques are grouped into the following major categories: (1) routine chemical field measurement techniques; (2) major sample extraction procedures; (3) analytical techniques that detect gases or require creation of a gaseous phase during the analytical process if the gaseous phase is not already present; (4) luminescence, spectrophotometric, and other spectroscopic techniques; (5) wet chemistry techniques; and (6) radiological and other miscellaneous techniques.

Photo and *flame ionization* detectors are used routinely in contaminant investigations to screen for the presence of volatile compounds. Portable instrumentation for *gas chromatography* has improved to the point where it can be considered a well-established field analytical method for site investigations involving organic chemicals. Portable *x-ray fluorescence* instruments are now commercially available for field screening of heavy metal contamination in soil and waste materials. *Colorimetric wet chemistry* field test kits for analysis of inorganic constituents are being increasingly accepted for use in EPA drinking water and National Pollutant Discharge Elimination System (NPDES) programs. Colorimetric *enzyme immunoassay* (EIA) test kits are a rapidly developing area of field chemical analysis. EIA kits have been developed for pentachlorophenol, explosives, and pesticides.

9.6.3 Types of Analytical Instrumentation

For the nonchemist, terminology used to describe analytical techniques can be bewildering. A further source of potential confusion is that techniques can be used for different purposes in numerous combinations and configurations. For example, a flame ionization detector (FID) can be used by itself as a total vapor detector, or it can be used to detect specific compounds after they have been separated by a gas chromatograph (GC/FID). A gas chromatograph, on the other hand, can be used alone with a FID or other type of detector, or in combination with a mass spectrometer (GC/MS). An understanding of the basic principles of operation of major individual techniques makes it possible to have some idea of how an unfamiliar combination of techniques functions.

A further source of possible confusion is that the different terms can be applied to the same technique. For example, the terms *fluorometry*, *fluorimetry*, and *spectrofluorometry* can be used interchangeably. Furthermore, some terms can be applied to the same technique, but are not necessarily interchangeable. For example, the term *luminescence* can be applied to any technique involving fluorescence, but the term *fluorescence* is not applicable to all luminescence techniques (which include phosphorescence). The following discussion might be helpful in developing an

Table 9.9 Major Analytical Signals and Methods

Signal	Analytical Methods Based on Measurement of Signal
Emission of radiation	Emission spectroscopy (x-ray, UV, visible, electron auger); fluorescence and phosphorescence spectroscopy (x-ray, UV, visible); radiochemistry
Absorption of radiation	Colorimetry (visible), UV-visible/x-ray/IR spectrophotometry ; photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy
Scattering of radiation	Turbidimetry, nephelometry, Raman spectroscopy
Refraction of radiation	Refractometry, interferometry, x-ray diffraction
Rotation of radiation	Polarimetry, optical rotatory dispersion, circular dichroism
Electrical potential	Potentiometry , chronopotentiometry
Electrical current	Polarography, amperometry, coulometry , voltammetry
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Kinetic methods
Thermal properties	Thermal conductivity and enthalpy methods
Mass	Gravimetric analysis
Volume	Volumetric analysis

Note: Boldface = most commonly used in field screening and analytical applications.

Source: Boulding (1993b), after Skoog (1985).

understanding of some of the basic principles involved in chemical analysis and in sorting out the relationships between similar techniques. It might also be helpful to think of techniques in terms of the major types of analytical signals, as summarized in Table 9.9.

Chromatography refers to processes in which individual components of a mixture migrate through a stationary medium at different rates. In analytical chemistry, chromatography refers to a diverse group of separation methods such as *gas chromatography* and *liquid chromatography* used to separate, isolate, and identify components of mixtures that might otherwise be resolved with great difficulty.

A *spectrum* is the distribution of the phases of a radiated wave cycle or of the intensity of radiation when some property (frequency, mass, or energy) is allowed to vary. *Spectroscopy* encompasses a wide range of techniques involving optical instruments used to form and analyze spectra. *Spectrometry* is a spectroscopic technique in which the instrument measures (1) the deviation of the refracted rays, and (2) wave lengths and angles between two faces of a prism. *Spectrophotometry* involves making comparisons of color intensity between corresponding parts of different spectra or between parts of the same spectrum. *Photometry* involves the measurement of the intensity of light or the relative intensity of different lights. *Luminescence* involves the emission of light at temperatures below those of incandescent bodies and includes *fluorescence* (emission of radiation as a result of absorption of other radiation) and *phosphorescence* (light given off from slow oxidation of phosphorus).

9.7 GUIDE TO MAJOR REFERENCES

Table 9.10 provides an index of major references dealing with the following general topics: (1) site investigations, (2) ground-water monitoring, (3) microbiological sampling, (4) vadose zone monitoring, (5) soil sampling, and (6) waste sampling. The table also indexes references according to agency or organization. Sara (2002) is recommended as a recent and comprehensive guide to facility assessments for solid and hazardous waste.

U.S. EPA (1986c) provides guidance on unsaturated zone monitoring. ASTM D4696 (Table A.14) provides more detailed guidance on selection and installation of soil-pore liquid sampling devices, and ASTM D5314 provides guidance on soil gas monitoring in the vadose zone. Aller et al. (1991) and Nielsen and Schalla (1991), the updated version of Aller et al., are good references

on design and installation of ground-water monitoring wells. Boulding (1991, 1994) are good references on the description and sampling of contaminated soils.

Table 9.11 provides an index of major references on field and laboratory methods for chemical and physical analysis of water, soil, sediment, chemical contaminants, other solid waste, and microbiology. The NFEC/EPA (1998) *Field Sampling and Analysis Technologies Matrix and Reference Guide* can be viewed at <www.frtr.gov>. The *Field Analytical Technologies Encyclopedia* (FATE) can be accessed at <fate.clu-in.org>. SW-846 (U.S. EPA, 1986b) is the standard reference for solid waste test methods. The latest version can be seen at <www.epa.gov/epaoswer/hazwaste/test/main.htm>.

Table 9.10 Index to Major Reference Sources on Subsurface Sampling and Monitoring Methods

Topic	References
Site Investigations	
General Methods	See Appendix B for available compilations of relevant ASTM standards <u>Expedited/Accelerated Site Characterization</u> : ASTM D6235 and E1912 (Table A.14), Burton et al. (1993 — ESC), Robbat (1997 — adaptive sampling), U.S. DOE (1998), U.S. EPA (1992d — SACM, 1997 — UST, 2001a, 2001b, 2001c — Triad approach, 2003 — DFA guidance), Waslenchuk and Man (1996 — STERDI); <u>ESC Case Studies</u> : Applegate and Fitton (1997), Burton (1994), Burton and Walker (1997), Burton et al. (1993, 1995), U.S. EPA (2000b), Waslenchuk and Man (1996); <u>Environmental Site Characterization</u> : ASCE (1999), ASTM (2002), ASTM D5730 (Table A.14), NFEC/EPA (1998); <u>Hydrologic Characterization</u> : Alley (1993), ASTM (1999a), Boulding (1993, 1996), Brakensiek et al. (1979), Brown et al. (1983), Bureau of Reclamation (1981), Dames & Moore (1974), Driscoll (1986), Johnson et al. (1997 — on-site septic systems), Kolm (1993), Liu and Liptak (1999), Nielsen and Johnson (1990), Nielsen and Sara (1992), Penn Inc. (1994), Rehm et al. (1985), Sara (2002), Thompson et al. (1989), UNESCO (1983), U.S. EPA (1991a, 1991b, 1993d), USGS (1977+), Van Haveren (1986), Waste Management of North America (1991), Zimmie and Riggs (1981); <u>Geotechnical Investigations</u> : Corps of Engineers (1984), Dowding (1978), Hanna (1985), Hathaway (1988), Jha (2000), Lambe (1951), Robertson and Mayne (1998), Saxena et al. (2001), USNFEC (1982); <u>Ecological Assessment</u> : See Table 11.10
Specific Settings	<u>EPA SOPs</u> : U.S. EPA (1991d, 1991e, 1996b); <u>Hazardous Waste Sites</u> : Cameron (1991), CCME (1994), Cochran and Hodge (1985), Ford and Turina (1985), Hazardous Materials Training and Research Group Staff (1997), Lesage and Jackson (1992), Oudjik and Mujica (1989), Perket (1986), Sara (2002), Sisk (1981), U.S. DOE (various dates), WPCF/WEF (1988); <u>DNAPL Sites</u> : Cohen and Mercer (1993), Pankow and Cherry (1996), U.S. EPA (1992c, 1993b); <u>EPA Superfund/CERCLA Sites</u> : U.S. EPA (1987, 1988c — RI/FS, 1991c — PA, 1991f — PA, 1991g — RI/FS for landfills, 1992b — SI, 1992e — HRS, 1993c — PA, 1996 — pre-CERCLIS, 1999a — PA, 1999b — pre-CERCLIS, 1999c — PA/SI, 2000a — combined removal action/RI); <u>EPA RCRA Facilities</u> : Cosgrove et al. (2000), U.S. EPA (1986d — RFA, 1989a — RFI, 1989b, 1993a); <u>Real Estate Environmental Assessments</u> : AGWSE (1992), ASTM (2000, 2001), Colangelo (1991), Environmental Resource Center (1993), Heijzlar (1999), Hess (1993), Hess-Cosa (1997), Jain et al. (1993), Vincoli (1993); <u>USTs/NAPL Sites</u> : Cheremisinoff (1992), Cohen and Mercer (1992), Cole (1994), Texas Water Commission (1993); <u>Low-Level Radioactive Wastes</u> : Byrnes (2000), EG&G (1990); <u>Remedial Operations</u> : Byrnes (1994), Cohen et al. (1994), Ross and Keeley (1992), U.S. EPA (1988a, 1991a); <u>Surface Impoundments</u> : Silka and Swearingen (1978); <u>Surface Mining</u> : Barrett et al. (1980)
Ground-Water Monitoring	
General Procedures	Collins and Johnson (1988), Crouch et al. (1976), Devinyy et al. (1990), EG&G (1990), Everett (1980), Everett et al. (1976), Fried (1975), Gillham et al. (1983), Keith (1992), Loftis and Ward (1979), Mooij and Rovers (1976), Morrison (1983), Nielsen (1991), Nielsen and Johnson (1990), Nielsen and Sara (1992), Ontario Ministry of the Environment (1989), Ross and Keeley (1992), Todd et al. (1976), U.S. DOE (various dates), U.S. EPA (1986b, 1990a, 1990b, 1991a, 1991b, 1993a), van Duijvenbooden and van Waegeningh (1987), Ward et al. (1990), WEF (1993/T4.4)
Drilling/Monitoring Wells	Aller et al. (1991), Anderson (1984), ASTM (1999b), Australian Drilling Industry Committee (1997), Barcelona et al. (1983), Campbell and Lehr (1973), Driscoll (1986), Harlan et al. (1989), Heinz (1985 — diamond drilling), Howsam (1990), Korte and Kearn (1985), Lehr et al. (1988), Mansuy (1998 — well rehabilitation), McCalou et al. (1995 — NAPL compatibility), Nielsen and Schalla (1991), Roscoe Moss Company (1990), Ruda and Bosscher (1990), Shuter and Teasdale (1989), Smith (1998 — water wells); <u>Prepacked Screens</u> : Geoprobe (1996)
Sampling Procedures	API (1987), Barcelona et al. (1983, 1985), Berg (1982), Classen (1982), Holden (1984), Keith (1988), Korte and Kearn (1985), Nash and Leslie (1991), Puls and Barcelona (1996 — low-flow sampling), Rainwater and Thatcher (1960), Scalf et al. (1981), Summers and Gherini (1987), Unwin (1982), Wilson (1995), Wood (1976)
Costs	Crouch et al. (1976), Everett et al. (1976), Loftis and Ward (1979)

Table 9.10 Index to Major Reference Sources on Subsurface Sampling and Monitoring Methods (Continued)

Topic	References
Specific Settings	Tinlin (1976); <u>Karst</u> : Quinlin (1989); <u>Solid Waste Disposal</u> : Fenn et al. (1977), U.S. EPA (1981a, 1981b, 1986f); <u>RCRA Facilities</u> : U.S. EPA (1983a, 1983b, 1985, 1986a, 1986d, 1986e, 1986f, 1989b); <u>Enhanced Oil Recovery</u> : Beck et al. (1981); <u>Surface Mining</u> : Everett (1979, 1983, 1985), Everett and Hoylman (1980a, 1980b), Williams and Schuman (1987); <u>Oil Shale</u> : Everett (1985), Slawson (1979, 1980a, 1980b); <u>Electric Utilities</u> : GeoTrans (1989), Redwine et al. (1985); <u>Wastewater and Sludge Application</u> : Ho et al. (1978); <u>Waste Spills</u> : Pilie et al. (1975), Yang and Bye (1979); <u>Geothermal</u> : Weiss et al. (1979); <u>WHPAs</u> : Moore (1993/T11.11)
State/Local Guidance Documents ^a	Connecticut Environmental Protection Agency (1983), Lindorff et al. (1987), NJDEP (1992), Santa Clara County Water District (1985), Stephens (1986)
Microbiological Sampling	
	Bitton and Gerba (1984), Board and Lovelock (1973), Bordner et al. (1978), Britton and Greeson (1989), Dunlap et al. (1977), Edwards (1993), USGS (1977+); see also Table 9.11
Vadose Zone Monitoring	
General	ASTM (1999a, 1999b), Everett and Wilson (1986), Everett et al. (1983), Nielsen and Johnson (1990), Nielsen and Sara (1992), Rehm et al. (1985), Rijtema and Wassink (1969), U.S. EPA (1986c), Wilson (1980), Wilson et al. (1995); <u>Review Papers</u> : Cullen (1995), Cullen et al. (1995), Everett et al. (1982, 1984), Wilson (1981, 1982, 1983)
Soil-Solute Sampling	Devinnny et al. (1990), Morrison (1983), Nash and Leslie (1991), Nielsen (1991), USGS (1977+), Wilson (1995)
Soil Gas	Devitt et al. (1987), Ford et al. (1984), Kerfoot and Barrows (1987), Marrin and Kerfoot (1988), U.S. EPA (1988b)
Soil Sampling	
Field Characterization	Blume et al. (1991), Boulding (1991, 1993, 1994), Brakensiek et al. (1979), Bureau of Reclamation (1974, 1990), Cameron (1991), Hodgson (1978), SCS (1971)
General Sampling	Acker (1974), Barth et al. (1989), Cameron (1966), Corps of Engineers (1972), Hodgson (1978), Hvorslev (1948, 1949), Keith (1992), Mason (1992), McKeague (1978), Mooij and Rovers (1976), SCS (1984), Tan (1995), U.S. DOE (various dates), U.S. EPA (1995a); <u>Sediments</u> : See Table 9.11
Sampling for Soil Contaminants	API (1987, 1992), Boulding (1991, 1994), EG&G (1990), Ford et al. (1984), Goodwin et al. (1982), Keith (1988), Lewis et al. (1991), Neckers and Walker (1952 — active sulfides), Scalf et al. (1981), Schweitzer and Santolucito (1984), U.S. EPA (1986b, 1988b, 1989b, 1991a), van Duijvenbooden and van Waegeningh (1987)
Waste Sampling	
Sampling	deVera (1980), Ford et al. (1984), Keith (1988, 1992), Rupp and Jones (1993), Simmons (1991), U.S. DOE (various dates), U.S. EPA (1986b, 1992a, 1995b), Wolbach et al. (1984)
Agency/Organization Index	
U.S. EPA	<u>Soils and Ground Water</u> : Aller et al. (1991), Cochran and Hodge (1985), Dunlap et al. (1977), Everett et al. (1976), Fenn et al. (1977), Ford and Turina (1985), Ford et al. (1984), Ross and Keeley (1992), Scalf et al. (1981), Silka and Swearingen (1978), Sisk (1981), U.S. EPA (1986d, 1987, 1989a, 1989a, 1989b, 1990b, 1991a, 1991c, 1991d, 1991e); <u>Vadose Zone</u> : Devitt et al. (1987), Everett et al. (1983), Kerfoot and Barrows (1987), U.S. EPA (1986c), Wilson (1980); <u>General Ground Water</u> : Barcelona et al. (1985), Berg (1982), Crouch et al. (1976), Loftis and Ward (1979), Tinlin (1976), Todd et al. (1976), U.S. EPA (1990a, 1991a), Yang and Bye (1979); <u>Ground-Water Guidance Documents</u> : U.S. EPA (1981a, 1981b, 1983a, 1983b, 1985, 1986a, 1986e, 1986f, 1988a, 1991e, 1992b, 1993); <u>NAPLs</u> : Cohen and Mercer (1993), U.S. EPA (1992b); <u>Soil and Solid/Liquid Waste</u> : Barth et al. (1989), Boulding (1991), Cameron (1991), deVera (1980), Hatayama et al. (1980), Mason (1992), Pilie et al. (1975), U.S. EPA (1986b, 1991e, 1992a), Yang and Bye (1979); <u>Energy Development Ground-Water Monitoring</u> : Beck et al. (1981), Everett (1979, 1983), Everett and Hoylman (1980a, 1980b); Slawson (1979, 1980a, 1980b), Weiss et al. (1979)

Table 9.10 Index to Major Reference Sources on Subsurface Sampling and Monitoring Methods (Continued)

Topic	References
Other Federal	<u>Bureau of Reclamation</u> : Bureau of Reclamation (1974, 1981, 1990); <u>Department of Energy</u> : EG&G (1990), U.S. DOE (various dates); <u>Fish and Wildlife Service</u> : Brown et al. (1991); <u>Forest Service</u> : Barrett et al. (1980); <u>NASA</u> : Cameron et al. (1966); <u>Navy</u> : UNSFEC (1982); <u>USATHAMA/Corps of Engineers</u> : Corps of Engineers (1972, 1984), Goodwin et al. (1982), Hvorslev (1949), Plumb (1981); <u>USDA/SCS</u> : Brakensiek et al. (1979), SCS (1971, 1984); <u>U.S. Geological Survey</u> : Classen (1982), Edwards and Glysson (1988), Guy (1969), USGS (1977+), Wood (1976)
Other Government	<u>Canada</u> : Carter et al. (1993/T9.11), CCME (1994), Mooij and Rovers (1976); <u>States</u> : ^a Barcelona et al. (1983), Connecticut Environmental Protection Agency (1983), Lindorff et al. (1987), NJDEP (1992), Stephens (1986)
American Society for Testing and Materials (ASTM)	ASTM (annual, 1992, 1997, 1999a, 1999b, 2000, 2001, 2002); <u>Ground-Water and Vadose Zone STPs</u> : Collins and Johnson (1988), Nielsen and Johnson (1990), Nielsen and Sara (1992), Zimmie and Riggs (1980); <u>Hazardous Waste Solid Testing Conference Series</u> : (Papers in this series tend to focus on laboratory methods, but also include papers on field-oriented techniques): 1st (Conway and Mallow, 1981); 2nd (Conway and Gullede, 1982); 3rd (Jackson et al., 1984); 4th (Petros et al., 1985); 5th (Perket, 1986); 6th (Lorenzen et al., 1986)
Other Organizations	<u>American Chemical Society (ACS)</u> : Keith (1988, 1992), Nash and Leslie (1991), Schweitzer and Santolucito (1984); <u>American Petroleum Institute (API)</u> : API (1987, 1992), Gillham et al. (1983); <u>Consulting Firms</u> : Dames and Moore (1974), Everett (1980), GeoTrans (1989), Waste Management of North America (1991); <u>Electric Power Research Institute (EPRI)</u> : EPRI (1985), Redwine et al. (1985), Rehm et al. (1985), Summers and Gherini (1987), Thompson et al. (1989); <u>UNESCO</u> : Brown et al. (1983), Rijtema and Wassink (1969), UNESCO (1983)

^a The appropriate state regulatory agency should be contacted for the most current version of any guidance documents.

Table 9.10 References (Appendix F contains references for figure and table sources.)

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* See Preface for information on how to obtain documents from CERI and NTIS.

Table 9.11 Index to Major References on Field and Laboratory Test and Analytical Methods

Topic	References
General	Csuros (1994, 1997), Csuros and Csuros (2002 — metals); <u>Instrumentation Principles</u> : Skoog (1985), Willard et al. (1988); <u>QA/QC</u> : AOAC (1975, 1985, 1991)
Field Screening and Analytical Methods	<u>U.S. EPA</u> : Crockett et al. (1996 — explosives in soil), Minnich (1993), NFEC/EPA (1998), U.S. EPA (1988, 1993); <u>Other</u> : Balshaw-Biddle et al. (1999 — laser fluorescence), Clement et al. (1992), CMECC (1996), Crockett et al. (1999 — explosives in water), Gammage and Berven (1992), NJDEPE (1994)
U.S. EPA Analytical Methods	<u>Overviews</u> : Keith (1996a, 1996b), Mueller and Smith (1991), Nelson (1988), Smith (1994), Wagner (1994); <u>General</u> : Kopp and McKee (1983); <u>Metals</u> : U.S. EPA (1991a); <u>Organics in Water</u> : Longbottom and Lichtenberg (1982); <u>Solid Waste (SW-846)</u> : U.S. EPA (1986b); <u>SW-846 Methods Studies</u> : Edgill (1989), Edgill and Wilburs (1989), Engel et al. (1988); <u>Drinking Water Analysis</u> : Long and Martin (1989), Pfaff (1981), U.S. EPA (1990a, 1990b, 1991d); <u>Pesticides</u> : U.S. EPA and State Laboratories (1993), Watts (1980); <u>Sediment</u> : Guy (1969), Plumb (1981), U.S. EPA (1989); <u>Quality Control</u> : Booth (1979), Provost and Elder (1985), Sharma (1979)
U.S. Geological Survey TWRIs (The Techniques of Water-Resources Investigation series includes manuals describing procedures for planning and conducting specialized work in water resources investigations.)	<u>Water</u> : Barnett and Mallory (1971 — minor elements), Britton and Greeson (1989 — aquatic biology and microbiology; supersedes Greeson et al., 1977), Fishman and Friedman (1989 — inorganic constituents; supersedes Brown et al., 1970; Skougstad et al., 1979; and Fishman and Bradford, 1982), Friedman and Erdman (1982 — quality assurance), Thatcher et al. (1977 — radioactive substances), Wershaw et al. (1987 — organic substances; supersedes Goerlitz and Brown, 1972), Wood (1976 — field analysis of unstable constituents); <u>Fluvial Sediment</u> : Fishman and Friedman (1989 — inorganic constituents; supersedes Brown et al., 1970; Skougstad et al., 1979; and Fishman and Bradford, 1982), Friedman and Erdman (1982 — quality assurance), Guy (1969 — physical analysis), Thatcher et al. (1977 — radioactive substances), Wershaw et al. (1987 — organic substances; supersedes Goerlitz and Brown, 1972)
Other Major References	
Water	<u>Standard Methods</u> : APHA (1995), ASTM (1966, annual — Vols. 11.01 and 11.02), Hach (1991), AOAC (1990); <u>Other Major References</u> : Crompton (1993), Fresenius et al. (1988), Nollet (2000), Rainwater and Thatcher (1960), Thompson et al. (1989), Velthorst (1993); <u>Injected Water/Waste Compatibility</u> : Collins and Crocker (1988), Ostroff (1965), Warner and Lehr (1977), Watkins (1954)
Soil	Baize (1993), Carter (1993), McKeague (1978), Smith and Mullins (1991, 2000), Tan (1995); <u>Physical Properties</u> : ASTM (annual — Vols. 4.08 and 4.09), Blume et al. (1991), Carter (1993), Klute (1986), SCS (1984), Smith and Mullins (1991, 2000), Stockham and Fochtman (1979 — particle-size analysis), Topp et al. (1992); <u>Clay/Other Mineralogy</u> : Carroll (1970), Johnson and Maxwell (1981), Kerr (1959), Moore and Reynolds (1989), see also Table 3.12; <u>Soil Chemistry</u> : Carter (1993), Council on Soil Testing and Plant Analysis (1992), Hoddinott and O'Shay (1993), Jackson (1958, 1979), Page et al. (1982), Sparks et al. (1996), van Lagen (1993), Walsh and Beaton (1990), Westerman (1990), see also Table 3.12; <u>Soil Microbiology/Biochemistry</u> : Page et al. (1982), Weaver et al. (1996)
Sediment	<u>Sampling</u> : ASTM D5387/TA.14, Barth and Starks (1985), Fleischauer and Engelder (1985), Murdoch and MacKnight (1994), Palmer (1985), Plumb (1981), U.S. EPA (1995), U.S. Interagency Committee (1940); <u>Analysis</u> : Edwards and Glysson (1988), Lichtenberg et al. (1988), Plumb (1981), U.S. EPA (1992 — contaminated sediment), U.S. Interagency Committee (1941), see also EPA and USGS TWRI references above
Contaminants	<u>Method Compilations</u> : Plumb (1984), U.S. DOE (various dates); <u>Ground Water</u> : API (1987 — petroleum hydrocarbons), Hach (1991 — inorganics), Lesage and Jackson (1992); <u>Hazardous Waste</u> : Francis et al. (1988), Silvestri et al. (1981), Wagner (1990), Wolbach et al. (1984); <u>Soil</u> : API (1987, 1992 — petroleum hydrocarbons), Minnich (1993 — VOCs), O'Shay and Hoddinott (1994); <u>Environmental Fate</u> : Howard et al. (1975), Mill et al. (1982)

Table 9.11 Index to Major References on Field and Laboratory Test and Analytical Methods (Continued)

Topic	References
Other Solid Waste	<u>Flue-Gas Desulfurization Waste</u> : Noblett and Burke (1990), Radian Corporation (1988); <u>Oil Shale</u> : Wallace et al. (1984); <u>Mine Soils and Overburden</u> : Williams and Schuman (1987)
Subsurface Microbiology	API (1965), Costerton and Colwell (1979), Ghiorse and Balkwill (1985), Pritchard and Bourquin (1984), Rosswall (1973), Weaver et al. (1996), Webster et al. (1985), see also references for microbiological sampling in Table 9.10

Table 9.11 References (Appendix F contains references for figure and table sources.)

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Use of Models and Computers in Contaminant Investigations

10.1 USES OF MODELS AND COMPUTERS

Models, in the broadest sense, are simplified descriptions of an existing physical system. Any soil or ground-water investigation that does more than simply collect and tabulate data involves modeling. A preliminary conceptual model, describing the soil and ground-water system, is tested by collecting data. If the data fit the preliminary model, it is accepted; otherwise, the model must be revised.

The meaning of the term *model* varies depending on the context in which it is used. Most models fall into one of the following categories:

- *Qualitative* descriptions of how processes operate in a system. For example, Table 3.10 and Figure 3.6 illustrate two qualitative models for biodegradation of organic contaminants.
- Simplified *physical* representations of the system such as “sand tank” physical aquifer models and laboratory batch experiments to measure adsorption isotherms (Section 4.5.2).
- *Mathematical* representations of a physical or chemical system.

This chapter focuses on models that can be expressed in mathematical form and adapted for use in computer codes. In this context, the American Society for Testing and Materials (ASTM) defines model and computer code as follows (ASTM D978/TA.14):

- A *model* is an assembly of concepts in the form of a mathematical equation that portrays understanding of a natural phenomenon.
- A *computer code* is the assembly of numerical techniques, bookkeeping, and control languages that represents the model from acceptance of input data and instruction to delivery of output.

The terms *computer* and *digital model* are often used interchangeably with *computer code*, but may also have a broader meaning to include the conceptual model of a site that forms the basis for entry of spatial and temporal data into a code. Computer codes may take the form of hard-paper documentation in the format of whatever programming language was used, or on an electronic medium (disks or tapes). Vadose zone and ground-water modeling with computers is a specialized field that requires considerable training and experience. In the last few decades, literally hundreds of computer codes for simulating various aspects of soil ground-water systems have been developed. Refinements to existing codes and development of new codes proceed at a rapid pace.

The great advantage of the computer is that large amounts of data can be processed quickly and experimental modifications can be made with minimal effort, so that many possible situations for a given problem can be studied in great detail. The greatest danger in computer modeling is that it is easy to generate outputs that have very little relationship to what is happening in the real world. [Section 10.4.6](#) identifies more specific potential pitfalls associated with computer modeling.

The major uses for computer modeling in the context of soil and ground-water contamination assessment and control can be broadly classified into (1) government decision making, (2) site assessment, and (3) ground-water protection and remediation. These categories are not mutually exclusive. For example, the results of modeling for site assessment, ground-water protection, and remediation all provide information for decision making.

10.1.1 Government Decision Making

Computers can assist government decisions concerning ground-water protection in the areas of (1) policy formulation, (2) rule making, and (3) regulatory action.

Policy Formulation. Modeling is not explicitly required in any federal water resource legislation, but is often the method of choice to assess the need for new legislation or the requirements of existing legislation (OTA, 1982/T10.6). The Netherlands and Israel have used computer modeling as a cornerstone in the development of ground-water protection policies (van der Heijde, 1985).¹ The U.S. EPA has used a generic vertical–horizontal spread (VHS) model to determine when solid waste needs to be treated as hazardous waste (National Research Council, 1990/T10.6).

Rule Making. The U.S. EPA's Underground Injection Program regulations on hazardous waste disposal injection restrictions and requirements for Class I wells exemplify the use of modeling to assist in rule making (Proposed Rules: 52 Federal Register 32446-32476, August 27, 1987; Final Rules: 53 Federal Register 28118-28157, July 26, 1988). The 10,000-year no-migration standard in 40 CFR 128.20(a)(1) for injected wastes is based, in part, on numerical modeling of contaminant transport in four major hydrogeologic settings by Ward et al. (1987).² Furthermore, worst-case modeling of typical injection sites by EPA formed the basis for the decision not to require routine modeling of dispersion in no-migration petitions.

Regulatory Action. Ground-water flow and possibly solute transport modeling are required to obtain a permit to inject hazardous wastes into Class I wells. Permitting decisions involving activities that may pose a threat to ground-water quality, such as landfills and surface storage of industrial wastes, commonly require ground-water simulations to demonstrate that no hazard exists.

10.1.2 Site Assessment

Use of modeling and computer codes can be valuable in two phases of site-specific soil and ground-water investigations: (1) site characterization and (2) exposure/risk assessment.

Site Characterization. Relatively simple models (such as analytical equations for ground-water flow that do not require use of computers — see Table 7.6) may be useful at the early stage for roughly defining the possible magnitude of a contaminant problem. Solute transport models that account for dispersion but not retardation ([Section 10.3.2](#)) may be useful in providing a worst-case analysis of the situation. They may help in defining the size of the area to be studied and in siting of monitoring wells. If more sophisticated computer modeling is planned, the specific code to be used will, to a certain extent, guide site characterization efforts by the aquifer parameters required as inputs to the model. Site characterization, particularly where water quality samples are tested

¹ van der Heijde, P.K.M. 1985. The Role of Modeling in Development of Ground-Water Protection Policies. Ground Water Modeling Newsletter 4(2).

² Ward, D.S., D.R. Buss, and J.W. Mercer. 1987. A Numerical Evaluation of Class I Injection Wells for Waste Confinement Performance, Final Report. Prepared for U.S. EPA by GeoTrans, Herndon, VA.

for possible organic contaminants, can generate large amounts of data. Computers are invaluable in compiling and processing these data sets ([Sections 10.5.2 and 10.5.6](#)).

Exposure and Risk Assessment. There is growing use of exposure assessments across the U.S. EPA's regulatory programs (U.S. EPA, 1988a, 1988b/T10.6). This application requires use of solute transport models that estimate the concentration of contaminants in ground water at points of potential exposure. In the case of ground-water contamination, the results of an exposure assessment will often determine whether remediation will be required. Section 11.4 discusses exposure and risk assessment methods in more detail.

10.1.3 Ground-Water Protection and Remediation

Computer models are useful for analyzing site and regional data to develop ground-water protection areas and to design ground-water cleanup systems.

Ground-Water Protection. Ground-water flow models are being increasingly used to assist in the process of delineating wellhead protection areas (WHPAs). About a dozen ground-water flow codes have been cited in the literature as having been used in actual wellhead delineation investigations. These codes fall into three general categories:

1. *Numerical* codes developed for general ground-water flow modeling (MODFLOW and USGS-2D FLOW) that are used to define zone of influence (ZOI), cone of depression (COD), and zone of contribution (ZOC)
2. Simpler analytical and semianalytical *capture zone* codes for defining the ZOI and ZOC of one or more pumping wells
3. Flow path analysis codes (called *path line tracing* or *reverse path*), typically analytical or semi-analytical, for calculating time of travel and velocity using the output from numerical modeling or capture zone codes

[Section 10.3](#) provides additional information on the classification of these codes. [Section 11.2](#) provides additional information on methods for delineating wellhead protection areas.

Remediation. Predictive models can be particularly valuable in estimating the possible effectiveness of alternative approaches to remediating ground-water contamination (Boutwell et al., 1985/T10.6). Chapter 12 discusses approaches to remediation. [Table 10.1](#) summarizes the type of modeling required for the following remediation design features: (1) capping, grading, and revegetation, (2) ground-water pumping, (3) wastewater injection, (4) interceptor trenches, (5) impermeable barriers, (6) subsurface drains, (7) solution mining, and (8) excavation.

10.2 MATHEMATICAL APPROACHES TO MODELING

Models and codes are usually described by the number of dimensions simulated and the mathematical approaches used. At the core of any model or computer code are *governing equations* that represent the system being modeled. Many different approaches to formulating and solving the governing equations are possible. The specific numerical technique embodied in a computer code is called an *algorithm*. The following discussion compares and contrasts some of the most important choices that must be made in mathematical modeling.

10.2.1 Deterministic vs. Stochastic Models

A *deterministic* model presumes that a system or process operates such that the occurrence of a given set of events leads to a uniquely definable outcome. The governing equations define precise cause-and-effect or input–response relationships. In contrast, a *stochastic* model presumes that a system or process operates such that factors contributing to an outcome are uncertain. Such

Table 10.1 Modeling Designed-System Alterations and Corrective Action

Design Feature	Effects on Ground Water	Type of Model Required	Typical Modeling Problems
Capping, grading, and revegetation	<ul style="list-style-type: none"> • Reduction of infiltration • Reduction of successive leachate generation • Changes in heads, direction of flow, and contaminant migration 	<ul style="list-style-type: none"> • Unsaturated zone model, vertical layered 	<ul style="list-style-type: none"> • Parameters related to leaching characteristics of reworked soil
Ground-water pumping (and optional reinjection of treated water)	<ul style="list-style-type: none"> • Controlled plume removal • Changes in heads and direction of flow 	<ul style="list-style-type: none"> • Saturated zone model, two-dimensional areal, axisymmetric or three-dimensional • Well or series of wells assigned to individual node 	<ul style="list-style-type: none"> • Representing partial penetration
Wastewater injection	<ul style="list-style-type: none"> • Plume generation • Changes in heads, direction of flow, and contaminant migration 	<ul style="list-style-type: none"> • Saturated zone model, two-dimensional area, axisymmetric or three-dimensional • Density-dependent flow • Temperature difference effects 	<ul style="list-style-type: none"> • Representing density-dependent effects
Interceptor trenches	<ul style="list-style-type: none"> • Plume removal 	<ul style="list-style-type: none"> • Saturated zone model, two-dimensional areal or cross-sectional, or three-dimensional • Trenches are represented by line of nodes with assigned heads 	<ul style="list-style-type: none"> • Representing partial penetration, resolution near trenches
Impermeable barrier (optional drainage system to prevent mounding)	<ul style="list-style-type: none"> • Containment of polluted water • Routing unpolluted ground water around site • Changes in heads and direction of flow 	<ul style="list-style-type: none"> • Saturated zone model, two-dimensional areal or cross-sectional, or three-dimensional • Possibly two-dimensional cross-sectional unsaturated zone model for liners 	<ul style="list-style-type: none"> • Representing partial penetration, flow and transport around end of barrier(s) • Conductivity liner or barrier material • Large changes in conductivity between neighboring elements • Differences in required grid resolution • Resolution near drain
Subsurface drains	<ul style="list-style-type: none"> • Removal of leachate • Changes in heads, direction of flow, and contaminant migration 	<ul style="list-style-type: none"> • Saturated or combined unsaturated-saturated zone model • Two-dimensional cross-sectional or three-dimensional 	
Solution mining	<ul style="list-style-type: none"> • Removal of contaminants after induced mobilization 	<ul style="list-style-type: none"> • Saturated or combined unsaturated-saturated zone model • Two-dimensional areal, cross-sectional or three-dimensional • Lines of sources (injection) and sinks (removal) 	<ul style="list-style-type: none"> • Parameters related to mobilization (sorption coefficient, retardation coefficient)
Excavation	<ul style="list-style-type: none"> • Removal of waste material and polluted soil • Changes in hydraulic characteristics and boundary conditions • Changes in heads and direction of flow 	<ul style="list-style-type: none"> • Unsaturated, saturated, or combined unsaturated-saturated zone model • For unsaturated, some models minimal one-dimensional vertical • For other types, minimal two-dimensional, cross-sectional 	<ul style="list-style-type: none"> • Parameters of backfill material

Source: Adapted by van der Heijde et al. (1988), from Boutwell et al. (1985).

models calculate the probability, within a desired level of confidence, of a specific value occurring at any point.

Most available models are deterministic. However, the heterogeneity of hydrogeologic environments, particularly the variability of parameters such as porosity and hydraulic conductivity, plays a key role in influencing the reliability of predictive ground-water modeling (Smith, 1987).³ Beven (1989)⁴ argues that this heterogeneity creates fundamental problems in the application of physically based deterministic models.

The governing equations for both deterministic and stochastic models can be solved either analytically or numerically (van der Heijde et al., 1988/T10.6). Vomvoris and Gelhar (1986/T10.6) provide some simple analytical examples of stochastic prediction of dispersive contaminant transport. Gómez-Hernández and Gorelick (1989)⁵ review the literature on approaches to stochastic simulation of ground-water model parameters such as hydraulic conductivity, leakance, and recharge, and Table 10.6 identifies other major references that address this topic.

10.2.2 System Spatial Characteristics

The spatial characteristics of a system can be modeled in two major ways. *Lumped-parameter* systems are used when the total system is located at a single point. *Distributed-parameter* systems define cause-and-effect relations for specific points or areas. *Input–response* or *black box* models do not explicitly address spatial characteristics, but instead empirically relate observations of different variables, such as response of water levels to recharge.

The distributed-parameter approach is most frequently used in ground-water modeling, and the rest of this chapter focuses on models of this type. The mathematical framework for distributed-parameter models includes (1) one or more partial differential equations called field equations, (2) initial and boundary conditions, and (3) solution procedures (Bear, 1979/T2.5). Depending on the solution method used, such models are characterized as analytical, semianalytical, or numerical (next section).

10.2.3 Analytical vs. Numerical Models

A model's governing equation can be solved either analytically or numerically. *Analytical* models use exact closed-form solutions of the appropriate differential equations. The solution is continuous in space and time. In contrast, *numerical* models apply approximate solutions to the same equations. *Semianalytical* models use numerical techniques to approximate complex analytical solutions, allowing a discrete solution in either time or space. Models using a closed-form solution for either the space or time domain and additional numerical approximations for the other domain are also considered semianalytical.

Analytical models provide exact solutions, but employ many simplifying assumptions concerning the ground-water system, its geometry, and external stresses in order to produce tractable solutions (Walton, 1984a/T10.7). This places a burden on the user to test and justify the underlying assumptions and simplifications (Javandel et al., 1984/T10.6).

Semianalytical models can provide streamline and travel time information through numerical or analytical expression in space or time. This information is especially useful for delineation of wellhead protection areas. *Analytic element models* are a relatively recent development in semianalytical modeling of regional ground-water flow. These use approximate analytic solutions by superposing various exact or approximate analytic functions, each representing a particular feature

³ Smith, L. 1987. The Role of Stochastic Modeling in the Analysis of Groundwater Problems. Ground Water Modeling Newsletter 6(1).

⁴ Beven, K. 1989. Changing Ideas in Hydrology: The Case of Physically-Based Models. Journal of Hydrology 105:157–172.

⁵ Gómez-Hernández, J.J. and S.M. Gorelick. 1989. Effective Groundwater Parameter Values: Influence of Spatial Variability of Hydraulic Conductivity, Leakance, and Recharge. Water Resources Research 24(3):405–419.

Table 10.2 Advantages and Disadvantages of Analytical and Numerical Methods

Advantages	Disadvantages
Analytical Methods	
1. Efficient when data on the system are sparse or uncertain	1. Limited to certain idealized conditions with simple geometry; may not be applicable to field problems with complex boundary conditions
2. Economical	2. Most cannot handle spatial or temporal variations in system
3. Good for initial estimation of magnitude of contamination	
4. Rough estimates often possible from existing data sources	
5. Input data for computer codes usually simple	
Numerical Methods	
1. Easily handled spatial and temporal variations of system	1. Achieving familiarity with complex numerical programs can be time-consuming and expensive
2. Easily handled complex boundary conditions	2. Errors due to numerical dispersion (artifacts of the computation process) may be substantial for transport models
3. Three-dimensional transient problems can be treated without much difficulty	3. More data input is usually required
4. Preparation of input data is usually time-consuming ^a	

^a Model-specific preprocessors ([Section 10.5.2](#)) and GIS/GSIS ([Section 10.5.5](#)) can greatly facilitate data input.

Source: Adapted from Boulding (1991b).

of the aquifer (Haitjema, 1985;⁶ Strack, 1987/T10.6; Haitjema, 1995/T10.6). A major advantage of these models is greater flexibility in incorporating varying hydrogeology and stresses compared to analytic models without significantly increasing the need for data (van der Heijde and Beljin, 1988/T10.6).

Numerical models are much less burdened by the simplifying assumptions used in analytical models and are therefore inherently capable of addressing more complicated problems, but they require significantly more input and their solutions are inexact (numerical approximations). For example, the assumptions of homogeneity and isotropicity are unnecessary because the model can assign point (nodal) values of transmissivity and storage. Likewise, the capacity to incorporate complex boundary conditions provides greater flexibility. The user, however, faces difficult choices regarding time steps, spatial grid designs, and ways to avoid truncation errors and numerical oscillations (Remson et al., 1971; Javandel et al., 1984/T10.6). Improper choices may result in errors unlikely to occur with analytical approaches (e.g., mass imbalances, incorrect velocity distributions, and grid-orientation effects). Table 10.2 summarizes the advantages and disadvantages of analytical and numerical models.

10.2.4 Grid Design

A fundamental requirement of the numerical approach is the creation of a grid that represents the aquifer being simulated (see [Figure 10.1](#)). This grid of interconnected nodes, at which process input parameters must be specified, forms the basis for a matrix of equations to be solved. A new grid must be designed for each site-specific simulation based on data collected during site characterization and the conceptual model that is developed for the physical system. Grid design is one

⁶ Haitjema, H.M. 1985. Modeling Three-Dimensional Flow in Confined Aquifers by Superposition of Both Two- and Three-Dimensional Analytic Functions. *Water Resources Research* 21(10):1557–1566.

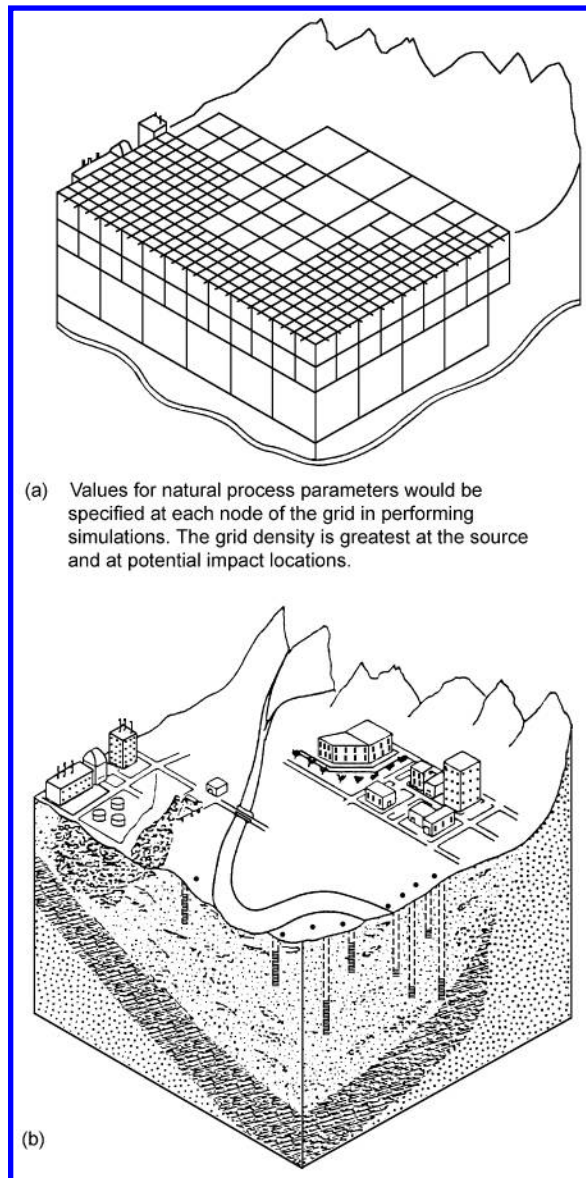


Figure 10.1 Three dimensional grid representing (a) a complex geologic setting (b) with pumping wells down-gradient from contaminant source (Keely, 1987).

of the most critical elements in the accuracy of computational results (van der Heijde et al., 1988/T10.6).

The grid design is influenced by the choice of numerical solution technique. Numerical solution techniques include (1) finite-difference (FD) methods, (2) integral finite-difference methods (IFDMs), (3) Galerkin and variational finite-element (FE) methods, (4) collocation methods, (5) boundary (integral) element methods (BIEMs or BEMs), (6) particle mass tracking methods, such as random walk (RW), and (7) the method of characteristics (MOC) (Huyakorn and Pinder, 1983/T10.6; Kinzelbach, 1986/T10.6). [Figure 10.2](#) illustrates grid designs involving FD and FE methods for the same well field.

Finite-difference and finite-element methods are the most frequently used numerical solution techniques. The finite-difference method approximates the solution of partial differential equations

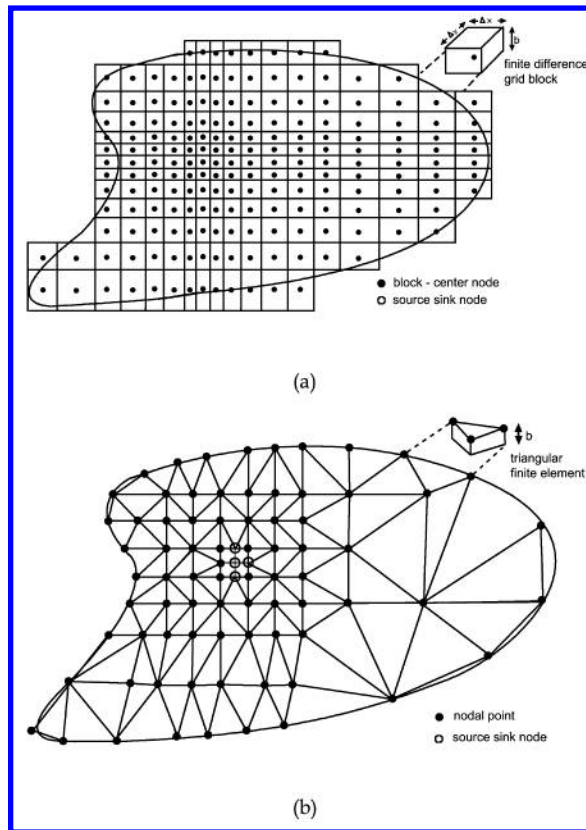


Figure 10.2 Comparison of (a) finite-difference and (b) finite-element grid configurations for modeling the same well field (Mercer and Faust, 1981).

by using finite-difference equivalents, whereas the finite-element method approximates differential equations by an integral approach. [Table 10.3](#) compares the relative advantages and disadvantages of the two methods. Most available numerical computer codes use finite-difference grids. Only in cases of highly irregular geometries do finite-element solutions have a clear advantage.

10.3 CLASSIFICATION OF GROUND-WATER COMPUTER CODES

Terminology for classifying vadose zone and ground-water computer codes according to the kind of system they simulate is sometimes inconsistent and confusing. There are so many different ways that such models can be classified (i.e., porous vs. fractured rock flow, saturated vs. unsaturated flow, mass flow vs. chemical transport, single phase vs. multiphase, isothermal vs. variable temperature) that a systematic classification cannot be developed that would not require placement of single codes in multiple categories.

The most comprehensive system for describing and classifying ground-water codes has been developed by the International Ground Water Modeling Center (IGWMC) (van der Heijde and Einawawy, 1993). This system uses four major categories for describing codes in IGWMC's database:

- *Model objectives*, such as applicability to certain types of ground-water management problems, and code development objectives (research, education, general use). [Section 10.1](#) discusses model objectives or uses further.

Table 10.3 Advantages and Disadvantages of Finite-Difference and Finite-Element Numerical Methods

Advantages	Disadvantages
Finite-Difference Method	
Intuitive basis	Low accuracy for some problems (mainly solute transport)
Easy data entry	Rectangular grids required
Efficient matrix techniques	
Programming changes easy	
Finite-Element Method	
Flexible grid geometry	Complex mathematical basis
High accuracy possible	More complex programming
Evaluates cross-product terms better	

Source: Adapted from Boulding (1991b).

- *Processes modeled*, such as saturated or unsaturated flow, solute transport and fate, and hydro-geochemical speciation.
- *Physical system characteristics modeled*, such as porous medium or fractured rock, single or multiple aquifers, confined or unconfined, etc.
- *Mathematical approaches*, such as general nature of equations (deterministic or stochastic) and solution method (analytical or numerical). [Section 10.2](#) discusses this aspect further.

[Table 10.4](#) presents a classification system for vadose zone and ground-water computer codes that is useful for evaluating models in relation to contaminant investigations. It combines elements of the process and physical system characteristics categories described above. The table has 4 major categories of codes and 11 major subdivisions that are discussed below. This classification scheme differs from others (see, for example, Mangold and Tsang, 1987; van der Heijde et al., 1988/T10.6) by distinguishing among solute transport models that simulate (1) only dispersion, (2) chemical reactions with a simple retardation or degradation factor, and (3) complex chemical reactions.

The literature on ground-water codes is most confusing when it comes to terminology for models that address subsurface chemistry. For example, the term *hydrochemical* has been applied to completely different types of codes. Rice (1986/T10.6) and van der Heijde et al. (1988/T10.6) used the term *hydrochemical* for codes in the hydrogeochemical category in [Table 10.4](#), whereas Mangold and Tsang (1987/T10.6) used the term *geochemical* for such models and the term *hydrochemical* to describe coupled geochemical and flow models (chemical reaction transport codes in [Table 10.4](#)). More recently, van der Heijde and Einawawy (1993/T10.6) have used the term *hydrogeochemical* for codes that model aqueous chemical reactions without regard to transport, and that term is used here. The major types of models are discussed briefly below.

10.3.1 Porous Media Flow Codes

Modeling of saturated flow in porous media is relatively straightforward; consequently, by far the largest number of codes are available in this category. Modeling variably saturated flow in porous media (most typically soils and unconsolidated geologic material) is more difficult because hydraulic conductivity varies with changes in water content in unsaturated materials. Such codes typically must model processes such as capillarity, evapotranspiration, diffusion, and plant water uptake. van der Heijde and Einawawy (1993/T10.6) provide summary information on porous media flow codes in the following categories (number in parentheses indicates number of codes): saturated flow/analytical (20); saturated flow/two-dimensional numerical (55); saturated flow/three-dimensional numerical (15); saturated flow/analytical inverse (aquifer test) models (29); saturated flow numerical inverse models (3); and saturated flow/path line models (20). Note that a single model

Table 10.4 Classification of Vadose Zone and Ground Water Flow and Transport Computer Codes

Type of Code	Description/Uses
Flow (Porous Media)	
Saturated	Simulates movement of water in saturated porous media; used primarily for analyzing ground-water availability
Variable saturated (vadose zone)	Simulates unsaturated flow of water in the vadose (unsaturated) zone; used in study of soil–plant relationships, hydrologic cycle budget analysis
Solute Transport (Porous Media)	
Dispersion	Simulates transport of conservative contaminants (not subject to retardation) by adding a dispersion factor into flow calculations; used for nonreactive contaminants such as chloride and for worst-case analysis of contaminant flow
Retardation/degradation	Simulates transport contaminants that are subject to partitioning or transformation by the addition of relatively simple retardation or degradation factors to create algorithms for advection-dispersion flow; used where retardation and degradation are linear with respect to time and do not vary with respect to concentration; vadose zone transport models of this type use variable-saturated flow governing equations with retardation/degradation factors
Chemical reaction	Combines an advection-dispersion code with a hydrogeochemical code (see below) to simulate chemical speciation and transport; <i>integrated</i> codes solve all mass momentum, energy transfer, and chemical reaction equations simultaneously for each time interval; <i>two-step</i> codes first solve mass momentum and energy balances for each time step, and then reequilibrate the chemistry using a distribution-of-species code; used primarily for modeling behavior of inorganic contaminants
Hydrogeochemical Codes	
Thermodynamic	Processes empirical data so that thermodynamic data at a standard reference state can be obtained for individual species; used to calculate reference state values for input into hydrogeochemical speciation calculations
Distribution of species (equilibrium)	Solves a simultaneous set of equations that describe equilibrium reactions and mass balances of the dissolved elements
Reaction progress (mass transfer)	Calculates both the equilibrium distribution of species (as with equilibrium codes) and the new composition of the water as selected minerals are precipitated or dissolved
Specialized Codes	
Fractured rock	Simulates flow of water in fractured rock; available codes cover the spectrum of advective flow, advection-dispersion, heat, and chemical transport
Heat transport	Simulates flow where density-induced and other flow variations resulting from fluid temperature differences invalidate conventional flow and chemical transport modeling; used primarily in modeling of radioactive waste and deep-well injection
Multiphase liquid flow	Simulates movement of immiscible fluids (water and nonaqueous phase liquids) in either the vadose or saturated zones; used primarily where contamination involves liquid hydrocarbons or solvents
Gas flow and vapor transport	Simulate liquid/gas phase changes and movement of vapors in the vadose zone

Source: Adapted from Boulding (1991b).

may fall into more than one category. The same report includes information on 25 variably saturated (vadose zone) flow numerical models and seven codes for estimating vadose zone flow parameters.

10.3.2 Porous Media Solute Transport Codes

Solute transport codes fall into three major categories (see Table 10.4 for descriptions): (1) dispersion codes, (2) retardation/degradation codes, and (3) chemical reaction transport codes. *Dispersion* codes differ from saturated flow codes only in having a dispersion factor and may be required if conservative contaminants such as nitrates are of potential concern. *Retardation/degra-*

ation codes are slightly more sophisticated because they add a retardation or degradation factor to the mass transport and diffusion equations. However, as discussed below, such codes must be used with caution. *Chemical reaction transport* codes are the most complex (but not necessarily most accurate) because they couple geochemical codes with flow codes. Chemical reaction transport codes may be classified as *integrated* or *two-step* codes (see [Table 10.4](#)).

Mechanisms for reducing the concentration of contaminants in an aquifer are generally too complex and difficult to predict for selection as criteria for wellhead protection (U.S. EPA, 1987).⁷ Accurate modeling of contaminant transport is limited by fundamental problems, including (1) inability to describe mathematically some processes, (2) complex mechanisms that are beyond the capability of available numerical techniques, and (3) difficulty in obtaining enough data of sufficient quality to calibrate models (van der Heijde and Beljin, 1988/T10.6).

Hydrodynamic dispersion, the process by which contaminants may travel *faster* than would be expected from simple ground-water flow calculations, must be considered when modeling for delineation of ground-water protection areas or for exposure assessment. As noted in Section 4.4.2, dispersion at the microscopic scale is such a minor component of ground-water movement that it can generally be ignored. Although dispersion at this scale results in a faster arrival time, it also reduces concentration levels and, consequently, can be considered an attenuating process. Transport of contaminants by macroscopic dispersion, on the other hand, is best addressed using methods that account for the effect of aquifer heterogeneity on the speed of ground-water flow (Sections 2.5.3 and 7.5.2). For simple methods, this would involve using the upper range of estimated or measured hydraulic conductivity in ground-water flow calculations. Numerical computer codes allow design of the grid to account for more highly transmissive layers.

Bradbury et al. (1991)⁸ provide a good example of the difference a single highly transmissive layer in an aquifer can make in travel times. At the Sevastopol site in Door County, Wisconsin, where the aquifer is in fractured dolomite, time of travel to the upgradient ground-water divide based on calculations using a potentiometric surface map was 100 years ([Figure 10.3](#)). Ground-water simulations using PATH3D that accounted for a fracture zone that was observed by hydro-geologic mapping to occur at a depth of 170 ft below the ground surface resulted in a travel time of 1 year from the ground-water divide ([Figure 10.4](#)).

Retardation processes (Section 4.5) provide an unstated safety factor to delineations based on advective flow to the extent that they diminish concentration as a contaminant moves through an aquifer. These codes are most commonly used in heavily contaminated settings to help develop remediation strategies. However, such codes may have value for wellhead protection as a means of quantifying the safety factor that is contained in delineations based on other methods or for further evaluation of the possible risks associated with potential contaminant sources within a wellhead protection area (Section 11.4).

In general, modeling of contaminant transport processes is more complex than modeling ground-water flow alone, and consequently, the results of any individual model should be viewed with caution. For example, Arnold (1992/T10.6) used eight numerical models and four analytical models to estimate attenuation of BTX (benzene, toluene, xylene) from a gasoline spill 4000 ft from the Mississippi River and found a two-order-of-magnitude range in the predicted concentrations.

van der Heijde and Einawawy (1993) provide summary information on solute transport codes in the following categories (number in parentheses indicates number of codes): saturated zone/analytical (42); saturated zone/two-dimensional numerical (38); saturated zone/three-dimensional numerical (20); and unsaturated zone (52).

⁷U.S. Environmental Protection Agency (EPA). 1987. Guidelines for Delineation of Wellhead Protection Areas. EPA/440/6-87-010 (NTIS PB88-111430). [R. Hoffer may also be cited as author]

⁸Bradbury, K.R., M.A. Muldoon, A. Zaporozec, and J. Levy. 1991. Delineation of Wellhead Protection Areas in Fractured Rocks. EPA/570/9-91-009, 144 pp.

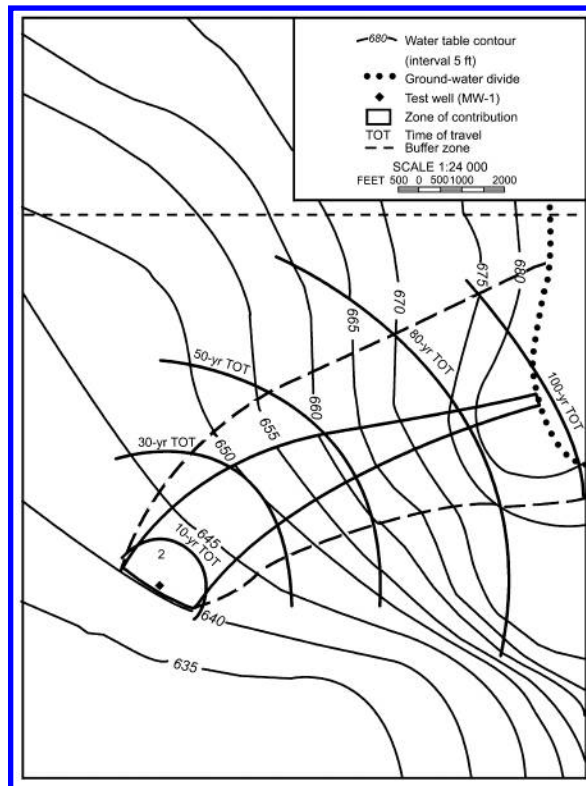


Figure 10.3 Time-of-travel contours in a dolomite aquifer based on potentiometric surface map (Bradbury et al., 1991).

10.3.3 Hydrogeochemical Codes

Hydrogeochemical codes simulate chemical reactions in ground-water systems without considering transport processes. These fall into three major categories (see Table 10.4): (1) thermodynamic codes, (2) distribution-of-species codes, and (3) reaction progress codes. By themselves, hydrogeochemical codes can provide qualitative insights into the behavior of contaminants in the subsurface. Chemical transport modeling of any sophistication requires coupling geochemical codes with flow codes (see previous section). Over 50 geochemical codes have been described in the literature (Nordstrom and Ball, 1984/T10.6); 27 are sufficiently documented to be summarized by van der Heijde and Einawawy (1993/T10.6).

10.3.4 Specialized Codes

This category contains special cases of flow codes and solute transport codes (see Table 10.4), including (1) fractured rock, (2) heat transport, (3) multiphase liquid flow, and (4) gas flow and vapor transport. *Fractured rock* creates special problems in the modeling of contaminant transport for several reasons. First, mathematical representation is more complex due to the possibility of turbulent flow and the need to consider roughness effects. Furthermore, precise field characterization of fracture properties that influence flow, such as orientation, length, and degree of connection between individual fractures, is extremely difficult. In spite of these difficulties, much work is being done in this area (Schmelling and Ross, 1989/T10.6); van der Heijde and Einawawy (1993) provide summary information on 31 fractured rock models, an increase of four models since IGWMC's previous compilation (van der Heijde et al., 1988/T10.6). It is worth noting that no fractured rock

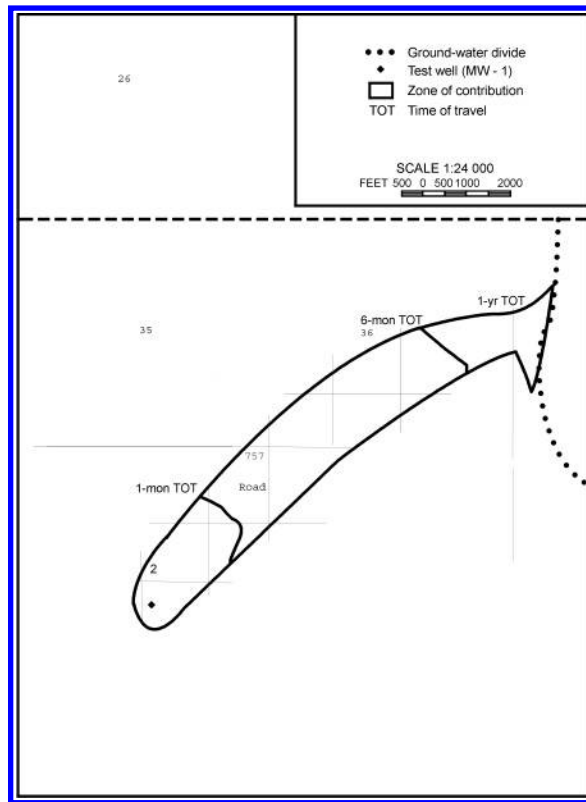


Figure 10.4 Time-of-travel contours in a dolomite aquifer based on numerical modeling of a high-conductivity zone (Bradbury et al., 1991).

models satisfied screening criteria developed by van der Heijde and Beljin (1988/T10.6) for codes potentially suitable for delineation of wellhead protection areas.

Heat transport models have been developed primarily in connection with enhanced oil recovery operations (Kayser and Collins, 1986/T10.6) and programs assessing disposal of radioactive wastes. Van der Heijde and Einawawy (1993/T10.6) present summary information on 51 heat transport models, an increase of 15 since IGWMC's 1988 survey. Early work in *multiphase fluid* flow centered in the petroleum industry focusing on oil–water–gas phases. In the last decade, multiphase behavior of nonaqueous phase liquids in near-surface ground-water systems has received increasing attention. However, the number of codes capable of simulating multiphase liquid flow is still limited, with van der Heijde and Einawawy (1993/T10.6) summarizing 12 codes. It is only relatively recently that the need for modeling *vapor phase transport* of volatile organic contaminants such as gasoline in the vadose zone has been recognized. This is especially important for design of remediation systems involving light nonaqueous phase liquids. This is a rapidly developing area of research, as demonstrated by the fact that 14 of the 18 gas flow and vapor transport listed by van der Heijde and Einawawy (1993) have been released since 1990.

10.4 GENERAL CODE SELECTION CONSIDERATIONS

All modeling involves simplifying assumptions concerning parameters of the physical system that is being simulated. Furthermore, these parameters will influence the type and complexity of the equations that are used to represent the model mathematically. Major considerations in selecting a computer code for a particular application include:

- Ground-water flow parameters (Section 10.4.1)
- Contaminant transport parameters (Section 10.4.2)
- Computer hardware and software (Section 10.4.3)
- Usability and reliability of the code (Section 10.4.4)
- Model quality assurance and quality control (Section 10.4.5)

Worksheet D-W5 can be used to develop PC-based ground-water computer code specifications and to evaluate code suitability for a specific site. Information on site characteristics should first be entered from Worksheets D-W1 (Water Well/Aquifer Data), D-W3 (Possible Aquifer Boundaries), and D-W4 (Aquifer Characteristics for the Selection of Analytical Solutions to Ground Flow in the Vicinity of Wells). Next fill out the section of Worksheet D-W5 on model system requirements.⁹ Make as many copies of the worksheet with the site and system information as codes to be evaluated and fill in the rest of the worksheet using information sources identified in the rest of this section and in Section 10.6. Final code selection will require a qualitative evaluation of the suitability of each code in relation to site characteristics and project objectives.

10.4.1 Ground-Water Flow Parameters

There are six major parameters of ground-water systems that must be considered when selecting a computer code for simulating ground-water flow: (1) type of aquifer (confined, unconfined, leaky), (2) matrix characteristics (porous, fractured), (3) degree of homogeneity and isotropy, (4) phases (density differences, NAPLs), (5) number of aquifers, and (6) flow conditions (steady or transient). Figure 10.5 provides a decision tree for selection of a ground-water flow code based on characteristics of the system.

Type of Aquifer. Confined aquifers with uniform thickness are easier to model than unconfined aquifers because the transmissivity (Section 2.6.2) remains constant.¹⁰ The thickness of unconfined aquifers varies with fluctuations in the water table, thus complicating calculations. Similarly, simulation of variable-thickness confined aquifers is complicated by the fact that velocities will generally increase in response to reductions in the distance between confining beds and will decrease in response to increases in these distances.

Matrix Characteristics. Flow in porous media is much easier to model than in rocks with fractures or solution porosity. This is because (1) equations governing laminar flow are simpler than those for turbulent flow, which may occur in fractures, and (2) porosity and hydraulic conductivity can be more easily estimated for porous media.

Homogeneity and Isotropy. Homogeneous and isotropic aquifers are easiest to model because their properties do not vary in any direction (Section 2.5.3). If hydraulic properties and concentrations are uniform vertically, and in one of two horizontal dimensions, a *one-dimensional* simulation is possible. Horizontal variations in properties combined with uniform vertical characteristics can be modeled in *two dimensions*. Most natural aquifers, however, show variation in all directions and, consequently, require *three-dimensional* simulation, which also necessitates more extensive site characterization data. The spatial uniformity or variability of aquifer parameters such as recharge, hydraulic conductivity, porosity, transmissivity, and storativity (Section 2.6) will determine the number of dimensions to be modeled.

Phases. Flow of ground water and contaminated ground water in which the dissolved constituents do not create a plume that differs greatly from the unpolluted aquifer in density or viscosity (see Section 4.4.3) is easier to simulate than multiple phases.

⁹ This section of the worksheet can actually be used two ways: (1) to determine whether a particular code can run on an existing computer system, and (2) to develop minimum specifications for a new computer system for a code or codes that have been identified as suitable for a particular site.

¹⁰ The statement here and in following discussions about relative complexity of models has more effect on those who develop codes than users. From the user's standpoint, more complex models may require more computer memory or be slower in performing calculations than models of simpler systems, but are not necessarily more complex to use.

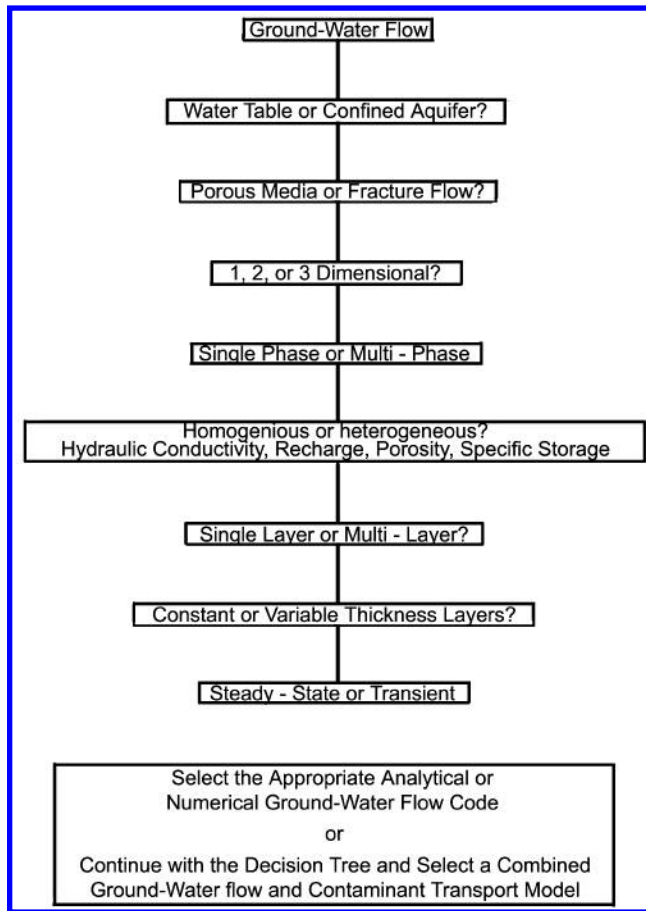


Figure 10.5 Decision tree for selection of ground-water flow code (U.S. EPA, 1988a).

Number of Aquifers. A single aquifer is easier to simulate than multiple aquifers.

Flow Conditions. *Steady-state* flow, where the magnitude and direction of flow velocity are constant with time at any point in the flow field, is much easier to simulate than transient flow. *Transient*, or unsteady flow, occurs when the flow varies in the saturated zone in response to variations in recharge or discharge rates. Both terms can also be applied to *unsaturated* flow in the vadose zone, also called *variably saturated* flow.

10.4.2 Contaminant Transport Parameters

Important contaminant parameters that should be considered when selecting a model for simulating transport or fate of contaminants include (1) concentration, (2) type of source (point, line, or areal), (3) type of source release (slug, continuous, constant, variable), (4) dispersion, (5) sorption, (6) degradation, and (7) density/viscosity effects. [Figure 10.6](#) provides a decision tree for selection of a contaminant transport model based on these factors.

Concentration. The simplest way to model contaminant transport in the subsurface is to specify a starting concentration in the ground water without considering the type of source.

Type of Source. For more sophisticated simulation purposes, sources can be characterized as point, line, area, or volume. A *point* source enters the ground water at a single point such as a pipe outflow or injection well and can be simulated with either a one-, two-, or three-dimensional model. An example of a *line* source would be contaminants leaching from the bottom of a trench. An *area*

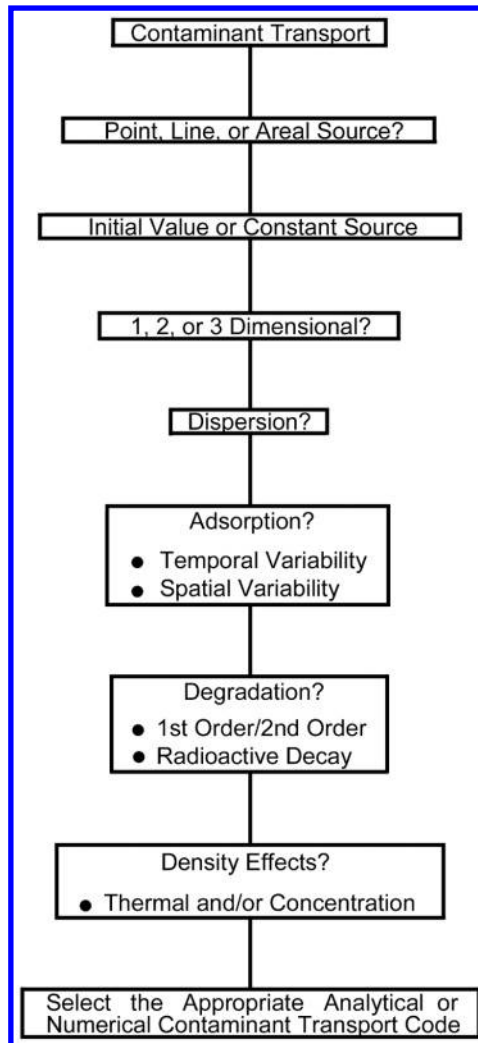


Figure 10.6 Decision tree for selection of contaminant transport code (U.S. EPA, 1988a).

source enters the ground water through a horizontal or vertical plane. The actual contaminant source may occupy three dimensions outside of the aquifer, but contaminant entry into the aquifer can be represented as a plane for modeling purposes. Leachate from waste lagoons and agricultural fields are examples of area sources. A *volume* source occupies three dimensions within an aquifer. A DNAPL that has sunk to the bottom of an aquifer (Figure 4.10) would be a *volume* source. Line and area sources may be simulated by either two- or three-dimensional models, whereas a volume source would require a three-dimensional model.

Type of Source Release. Release of an instantaneous pulse, or *slug*, of contaminant is easier to model than a *continuous* release. A continuous release may be either *constant* or *variable*. Figure 4.7b and Figure 4.8b show different contaminant plume configurations resulting from continuous and slug releases, respectively, and Figure 4.15 illustrates some effects of variations in the rate of release on contaminant plume shape.

Dispersion. Accurate contaminant modeling requires incorporation of transport by dispersion (Section 4.4.2). Unfortunately, the conventional convective-dispersion equation often does not accurately predict field-scale dispersion (U.S. EPA, 1988/T10.6) which typically requires numerical modeling of aquifer heterogeneity.

Adsorption. It is easiest to simulate adsorption with a single distribution or partition coefficient (Section 4.5.2). Nonlinear adsorption and temporal and spatial variation in adsorption are more difficult to model.

Degradation. As with adsorption, simulation of degradation is easiest when using a simple first-order degradation coefficient. Second-order degradation coefficients, which result from variations in various parameters such as pH, substrate concentration, and microbial population, are much more difficult to model. Modeling of radioactive decay is complicated but easier to simulate with precision because decay chains are well known.

Density/Viscosity Effects. If temperature or salinity of the contaminant plume is much different than that of the pristine aquifer, simulations must include the effects of density and viscosity variations (see Section 4.4.3).

10.4.3 Computer Hardware and Software

The types of computer hardware (model, random access memory (RAM), available use, peripherals for printing code output, etc.) that are available is a primary consideration in selecting a ground-water computer code. Earlier codes depended heavily on mainframe computers (such as CDC, IBM, PRIME, UNIVAC, and VAX models). Rapid advances in microcomputer technology have resulted in most ground-water modeling software being available for use on personal computers.¹¹ This trend stems from significant improvements in the computing power and quality of printed outputs obtainable from personal computers. It is also due to the improved telecommunications capabilities of personal computers, which are now able to emulate the interactive terminals of large business computers so that vast computational power can be accessed and the results retrieved with no more than a phone call.

Many of the mathematical models and data packages have been “ported” or rewritten from mainframe computers to personal computers. Most codes are now being written directly for this market. Table 10.7 provides an index to more than 50 public domain and commercially available PC-based vadose zone and ground-water flow and contaminant transport codes. A major advantage of PC-based codes is the relatively low cost of both hardware (the necessary computer and peripherals can probably be obtained for less than \$3000) and software. Most of the codes identified in Table 10.7 can be obtained for less than \$100, and most others for \$500 or less. Recent software catalogs should be consulted for the latest information on available codes (see Section 10.6).

10.4.4 Usability and Reliability

An ongoing program at the International Ground Water Modeling Center evaluates codes using performance standards and acceptance criteria (van der Heijde, 1987).¹² The IGWMC rates codes that are in its database using six *usability* and four *reliability* criteria. Favorable ratings for the usability criteria include:

- *Pre- and Postprocessors.* Code incorporates one or more of this type of code.
- *Documentation.* Code has an adequate description of user’s instructions and sample problems using example data sets.
- *Hardware Dependency.* Code is designed to function on a variety of hardware configurations.
- *Support.* Code is supported and maintained by the developers or marketers.

Favorable ratings for the reliability criteria include:

¹¹ Most first-generation software for microcomputers was developed for DOC-based IBM PC/AT/XT and compatibles and typically requires 640 KB (kilobyte) RAM. Second-generation DOS-based software typically requires a 386 or 486 CPU (central processing unit) with a math coprocessor and 2 MB (megabyte) RAM. Most sophisticated modeling software now requires Microsoft Windows with a pentium processor and 32 MB RAM.

¹² Van der Heijde, P.K.M. 1987. Performance Standards and Acceptance Criteria in Groundwater Modeling. Ground Water Modeling Newsletter 6(2).

- *Review*. Both theory behind the coding and the coding itself are peer reviewed.
- *Verification*. Code has been verified (see next section below).
- *Field Testing/Validation*. Code has been extensively field tested for site-specific conditions for which extensive data sets are available.
- *Extent of Use*. Code has been used extensively by other modelers.

Van der Heijde and Einawawy (1993) provide ratings for several hundred models.

10.4.5 Quality Assurance/Quality Control

The increasing use of modeling and computer codes in regulatory settings where decisions may be contested in court requires careful attention to quality assurance and quality control in both model development and application. There are three major aspects to quality control for a site-specific application of a model (ASTM D5447/TA.14):

1. *Sensitivity* is a measure of the degree to which model results are affected by changes in selected input parameters such as hydraulic properties.
2. *Calibration* is the process of refining input parameters that represent the hydrogeologic system being modeled to achieve a desired degree of correspondence between the simulation and observations of the actual system.
3. *Verification* requires that a code give results that are in reasonable agreement with analytical solutions or other computer codes using the same data. Verification in a model application requires that a calibrated model successfully simulate a second set of field data measured under similar hydrologic conditions.

These levels of quality control address the soundness and utility of the model alone and do not treat questions of its application to a specific problem. Hence, at least two additional levels of quality control appear justified:

4. Critical review of the problem's conceptualization to ensure that the modeling effort considers all physical, chemical, and biological processes that may affect the problem.
5. Evaluation of the specifics of the application, e.g., appropriateness of the boundary conditions, grid design, time steps, etc. Calibration and sensitivity analysis to determine if the model outputs vary greatly with changes in input parameters are important aspects of this process.

The term *validation* has sometimes been used in the ground-water modeling literature to refer to the highest level of QA/QC in which a model has been verified using real-world simulations in multiple locations. However, this term has been the subject of some recent controversy. Bredehoeft and Konikow (1993)¹³ suggested abandoning use of the term *validation* by the ground-water modeling community because it implies a precision that is not achieved in reality. In response, McCombie and McKinley (1993)¹⁴ argued that the term *validation* is appropriate for describing the process of guaranteeing that mathematical models “ensure an acceptable level of predictive accuracy.”

When model results are relatively insensitive to changes in values for input parameters, the accuracy of the input values is less of a concern than when a small change in an input parameter causes a large change in the model output. *Sensitivity testing* may be useful in guiding data collection for a site. Less attention need be given to estimating or measuring parameters that do not greatly affect the outcome of the modeling, whereas additional effort may be required to ensure that sensitive input parameters are measured accurately.

Whether the code has been verified or validated is an important criterion for selecting models. Verification is also desirable for site-specific applications, if it is possible to obtain a second set of field data measured under similar hydrologic conditions to the site-calibrated code. The code can

¹³ Bredehoeft, J.D. and L.F. Konikow. 1993. Ground-Water Models: Validate or Invalidate. *Ground Water* 21(2):178–179.

¹⁴ McCombie, C. and I. McKinley. 1993. Validation: Another Perspective. *Ground Water* 31(4):530–531.

be considered verified if it acceptably approximates the second data set. This can be determined by defining an acceptable level of departure between simulated values and the actual data set and calculating the difference between actual and simulated values (residuals). If these residuals fall within the range that was defined as acceptable, the model can be considered verified for application to that particular field situation.

Field validation of a numerical model consists of first calibrating the model using one set of historical records (e.g., pumping rates and water levels from a certain year), and then attempting to predict the next set of historical records. In the calibration phase, the aquifer coefficients and other model parameters are adjusted to achieve the best match between model outputs and known data; in the predictive phase, no adjustments are made (excepting actual changes in pumping rates, etc.).

Presuming that the aquifer coefficients and other parameters were known with sufficient accuracy, a mismatch means that either the model is not correctly formulated or that it does not treat all of the important phenomena affecting the situation being simulated (e.g., does not allow for leakage between two aquifers when this is actually occurring). Field validation is completed by conducting a *postaudit*, in which the predicted changes in responses to changes in the system are confirmed by field measurements.

10.4.6 Potential Pitfalls

Computers can easily give a false sense of security or cause unwarranted confidence in the results. The adage “garbage in, garbage out” always applies. Use of the criteria described previously for selection of a code that is appropriate for a particular objective and site conditions should reduce the chances that simulations result in “garbage out.” Nevertheless, it is useful to keep in mind pitfalls that can doom a ground-water modeling effort to failure (OTA, 1982; van der Heijde et al., 1985/T10.6):

- Inadequate conceptualization of the physical system, such as flow in fractured bedrock
- Use of insufficient or incorrect data
- Incorrect use of available data
- Use of invalid boundary conditions
- Selection of an inadequate computer code
- Incorrect interpretation of the computational results
- Imprecise or wrongly posed management problems

Computer modeling requires expertise in both hydrogeology and computer technology. The technology and software may be more readily available than the expertise. When in doubt, experts in government, universities, or consultants with special expertise in computer modeling of ground water should be consulted.

Subcommittee D18.21 on Vadose Zone and Ground-Water Investigations of the American Society for Testing and Materials (ASTM) has developed more than a dozen Standard Guides that cover various aspects of subsurface fluid flow modeling (see Appendix B). The first to be approved, *Standard Guide for Application of a Ground-Water Flow Model to a Site-Specific Problem* (D5447/TA.14), provides a good starting point for planning an investigation where computer modeling is going to be used.

10.5 OTHER GEOENVIRONMENTAL COMPUTER APPLICATIONS

In addition to modeling of vadose zone and ground-water flow and contaminant transport, other uses of computers for the assessment of soil and ground-water contamination include (1) parameter identification codes for estimation of vadose zone and aquifer properties, (2) code pre- and postprocessors to facilitate data entry and simulation outputs, (3) statistical analysis of

characterization and monitoring data, (4) simple graphical analysis and presentation of data, (5) geographic and geoscientific information systems (GIS/GSIS), and (6) neural networks and automated image processing.

10.5.1 Parameter Identification

Parameter identification codes are most often used to estimate the aquifer parameters determining fluid flow and contaminant transport characteristics. Examples of such codes include annual recharge (Puri, 1984),¹⁵ coefficients of permeability and storage (Shelton, 1982; Khan, 1986a, 1986b),¹⁶ dispersivity (Güven et al., 1984; Strecker and Chu, 1986),¹⁷ transmissivity and leakage factors for leaky confined aquifers (Mukhopadhyay, 1988),¹⁸ and watershed parameters (Rajaram and Georgakakos, 1989).¹⁹ Parameter estimation codes should *not* take the place of critical evaluation and interpretation of site data.

10.5.2 Code Pre- and Postprocessors

Data manipulation codes specifically designed to facilitate ground-water modeling efforts are becoming increasingly popular, because they simplify data entry (*preprocessors*) and facilitate the production of graphic displays of simulation results (*postprocessors*). Preprocessors can be designed for use with a specific code (e.g., Moses and Herman, 1986)²⁰ or for generic use. An early example of a generic preprocessor is PIG (Srinivasan, 1984).²¹ Commercial marketing of popular public domain ground-water models, such as USGS's MODFLOW, is typically based on pre- and post-processors that have been added to the code.

10.5.3 Statistical Analysis

Computers greatly ease statistical analysis by making it possible to perform rapid calculations using multiple statistical tests to a data set. Refer to Section 5.6 for discussion of basic statistical concepts. Major types of statistical analysis in soil and ground-water investigations include (1) trend analysis of time-series ground-water quality monitoring data, (2) multivariate and geostatistical analysis of spatial data, and (3) analysis of chemical analytical data for quality assurance/quality control purposes. Table 10.7 identifies EPA-developed statistical software. The rest of this section provides brief descriptions of major EPA software (refer to Table 10.7 for full citations).

The U.S. EPA's **GRITS/STAT** (Ground Water Information Tracking System with Statistical Analysis Capability) software functions as a database for ground-water quality monitoring data and performs the statistical tests recommended by EPA for analysis of ground-water monitoring data at RCRA facilities (U.S. EPA, 1992/T10.7). It is available from EPA's Center for Environmental Research Information (see Preface for address).

¹⁵ Puri, S. 1984. Aquifer Studies Using Flow Simulations. *Ground Water* 22(5):538–543.

¹⁶ Shelton, M.L. 1982. Ground-Water Management in Basalts. *Ground Water* 20(1):86–93. Khan, I.A. 1986a. Inverse Problem in Ground Water: Model Development. *Ground Water* 24(1):32–38. Khan, I.A. 1986b. Inverse Problem in Ground Water: Model Application. *Ground Water* 24(1):39–48.

¹⁷ Güven, O., F.J. Molz, and J.G. Melville. 1984. An Analysis of Dispersion in a Stratified Aquifer. *Water Resources Research* 20(10):1337–1354. Strecker, E.W. and W. Chu. 1986. Parameter Identification of a Ground-Water Contaminant Transport Model. *Ground Water* 24(1):56–62.

¹⁸ Mukhopadhyay, A. 1988. Automated Computation of Parameters for Leaky Confined Aquifers. *Ground Water* 26(4):500–504.

¹⁹ Rajaram, H. and K.P. Georgakakos. 1989. Recursive Parameter Estimation of Hydrologic Models. *Water Resources Research* 25(2):281–294.

²⁰ Moses, C.O. and J.S. Herman. 1986. Computer Notes: WATIN: A Computer Program for Generating Input Files for WATEQF. *Ground Water* 24(1):83–89.

²¹ Srinivasan, P. 1984. PIG: A Graphic Interactive Preprocessor for Ground-Water Models. GWMI 84-15, International Ground Water Modeling Center, Butler University, Indianapolis.

Geo-EAS (Geostatistical Environmental Assessment Software) is a collection of interactive software tools for performing two-dimensional geostatistical analyses of spatially distributed data (Englund and Sparks, 1991/T10.7). It was developed by EPA's Environmental Monitoring Systems Laboratory in Las Vegas (EMSL/Las Vegas, P.O. Box 93478, Las Vegas, NV 89193-3478) and includes programs for data file management, data transformations, univariate statistics, variogram analysis, cross-validation, kriging, contour mapping, post plots, and line/scatter graphs in a user-friendly format. **GEOPACK** (Yates and Yates, 1990/T10.7) is a competing geostatistical package developed by EPA's R.S. Kerr Environmental Research Laboratory (see address for CSMoS in [Section 10.6](#)). It performs geostatistical tests similar to those of Geo-EAS and also calculates a number a basic statistical parameters such as the mean, median, variance, standard deviation, etc. Each package is available from the respective EPA laboratory or the International Ground Water Modeling Center (address in [Section 10.6](#)).

EPA's **ASSESS** software (U.S. EPA, 1991a/T10.7), developed for EPA's Environmental Monitoring Systems Laboratory in Las Vegas, performs statistical analysis of regular soil samples and QA/QC samples (duplicates, replicates, etc.) to help evaluate whether data quality objectives are being met in sampling at hazardous waste sites. It is available from EPA's EMSL Las Vegas Laboratory (address above).

10.5.4 Data Plotting and Other Graphics

Computers can be used to present spatially related site data in a variety of forms:

- Maps that show the boundaries, surface topography, cultural features, and sampling points at a site
- Borehole soil or lithologic logs that describe characteristics or changes in soil or geologic materials with depth
- Monitoring well construction logs that document materials and methods used for constructing ground-water monitoring wells
- Cross sections and fence diagrams developed from lithologic, geophysical, or other types of subsurface information that provide a two- or three-dimensional view of lateral changes in soils and lithology in the subsurface
- Isopleth maps that show contours of equal concentration of contaminants or other parameters of interest and maps that represent data as contours (i.e., subsurface maps that show elevation contours of key lithologic units such as bedrock, clay, or sand layers)
- Volumetric data presentations, such as isopach maps, which show variations in the thickness of a horizon or strata, and three-dimensional portrayals of contaminant plumes in ground-water or zones of contamination in soil

Contour maps, lithologic logs, cross sections, and isopleth maps are essential elements in developing a conceptual model of a site that provides a basis for such undertakings as developing grids and input values for numerical computer models of a site, deciding whether remedial action is required, or selecting the location of permanent ground-water monitoring points for a detection monitoring program. Volumetric data are especially important for design of remediation systems at contaminated sites.

Dozens of commercial software packages of differing sophistication, cost, and complexity are available that facilitate the management, reporting, and analysis of temporal, spatial ground-water, and soils/geologic data. An assessment of data needs for development of EPA software for handling soils and geologic data as a complement to the GRITS/STAT software ([Section 10.5.3](#)) identified the following major commercial software as having a high potential for developing import/export utilities compatible with GEOS:²²

²² Boulding, J.R. 1993. Needs Document and Functional Specifications for the Proposed GEOS Module of the GRITS/STAT System. Prepared by Eastern Research Group, Inc., for U.S. EPA Center for Environmental Research Information, Cincinnati, OH, September 30. Note that funding limitations prevented full implementation of the GEOS module.

GEOBASE is available as a basic package for use in creating site maps, borehole log diagrams, well construction logs, and geological cross sections. The Advanced Lithology Package allows the customizing of logs, use of digitized geophysical logs, and creation of contour maps and fence diagrams. The database has some capability to sort records by data. Basic and advanced chemistry packages provide graphical analysis of sample data and can create isopleth maps. Maps can be digitized or DXF files imported. Some programs allow spreadsheet data entry, and all programs can read ASCII files.

Geotechnical Graphics System (GTGS) is a database that readily imports ASCII files, digitized maps, and widely used database and spreadsheet programs. Graphic outputs include site maps; customized lithologic, geophysical, and well construction logs; cross sections; and fence diagrams. The GTGL script language provides programming flexibility for customizing graphics and preparing tables. GTLog is a downsized version of GTGS for creating lithologic and well construction logs. Graphics created with this version can be exported to most commonly used word processing and graphics programs.

gINT is a database that allows creation of customized lithologic, geophysical, and well construction logs; geologic cross sections; fence diagrams; and contouring. It also can be used to graph data and to print data tables. It imports ASCII files and exports to ASCII, HPGL, or Lotus 1-2-3 WKS formats.

GISKey integrates elements of existing software (e.g., AutoCAD, Fox database, QUICKSURF) for analysis of site characterization and monitoring data. Graphic outputs include boring logs, cross sections, fence diagrams, and contour/isopleth and isopach maps. It handles QA/QC requirements for EPA's Contract Laboratory Program (CLP).

ROCKWORKS is an integrated collection of earth science software that is also available separately. Major components include DIGITIZE (a map, log, and general digitizing utility); GRIDZO (a relatively sophisticated gridding and contouring program); LOGGER (develops lithologic logs, cross sections, and fence diagrams); ROCKBASE (for creating base maps); ROCKSOLID (for carving out three-dimensional modeling and volumetric calculations); and ROCKSTAT (for making various statistical calculations). Graphics files can be exported to PCX, ASCII line, DXF, Postscript, HPGL, and PCL formats. The software imports ASCII line and HPGL files.

SPASE is a spatial database manager that runs in a Windows environment and allows the mapping and graphing of data. Contouring is done with mapping programs such as SURFER and GRIDZO (described elsewhere). **Image Spase** is used to capture or import digitized images. The software can import ASCII files and USGS DLG files (Digital Line Graph) and export files to a variety of programs. Other add-ons to the basic SPASE software include **Petro Spase**, oriented to oil and gas exploration and production, and **Enviro Spase**, which will soon be released for management of site characterization and monitoring data.

StratiFact is a spatial database that creates borehole logs, well construction logs, cross sections, contouring, and three-dimensional fence diagrams. Special features include the ability to plot the elevations of boreholes that deviate from the vertical, and to plot geologic cross sections of surface exposures.

10.5.5 Geographic Information Systems

Geographic information systems (GIS) use a common spatial framework for data input, storage, manipulation, analysis, and display of geographic, cultural, political, environmental, and statistical data.²³ Computer processing of spatial data can range from the use of relatively simple graphics software that can plot contours or isopleths from data for which x and y coordinates are known using ASCII or other data files (Section 10.5.4) to complex systems that can process digitized map data, maintain and manipulate large spatial databases, and generate a wide variety of user-created tables, graphs, and maps (Figure 10.7). This book uses the term *full-scale GIS* to refer to the type of integrated system illustrated in Figure 10.7, and *mini-GIS* to refer to personal computer (PC)-based software that is able to perform most of the functions of full-scale GIS at the scale of a

²³ The term *geoscientific information system* (GSIS) is also sometimes used.

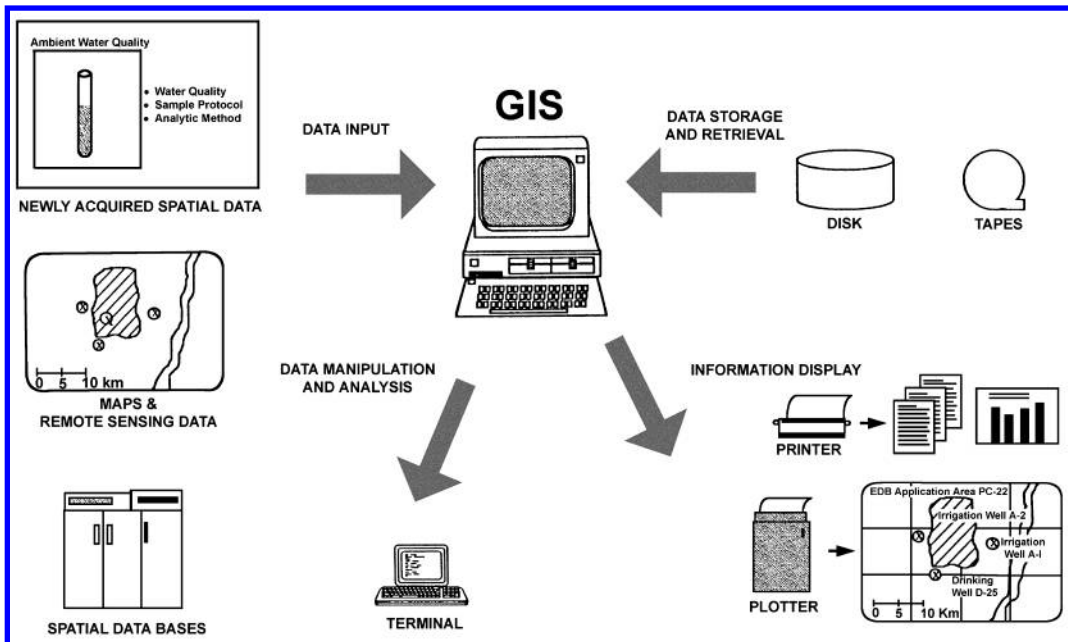


Figure 10.7 Overview of major geographic information system functions (OIRM, 1992).

USGS 7.5-min quadrangle (discussed further below) as an integrated package.²⁴ The term *desktop GIS* applies to the use of independent pieces of PC-based software to achieve the same results that full-scale and mini-GIS systems perform. Table 10.5 identifies major conferences and symposia with papers relevant to geographic information systems and journals focusing on this topic. Table 10.8 provides an index to more than 70 major GIS references.

Full-Scale GIS. The large amount of data that is stored and processed using full-scale GIS requires a workstation or mainframe computer environment with dedicated personnel for data entry and management. The costs of a full-scale geographic information system are substantial, but the greatest cost is the required commitment of personnel for data entry and management.²⁵ Consequently, the use of full-scale GIS is usually limited to large-scale projects or where GIS coverage of a site has been developed for other purposes. For example, Baker et al. (1993)²⁶ and Rifai et al. (1993)²⁷ have described use of the semianalytical WHPA code (Blandford and Huyakorn, 1991/T10.7) in conjunction with full-scale GIS in Rhode Island and Texas, respectively. The Massachusetts Water Resources Authority, which supplies water to 46 communities in Metropolitan Boston, has used GIS to delineate critical recharge areas for local supplies and mapped thousands of point and nonpoint potential sources of contamination (Brandon et al., 1992).²⁸ Pickus (1992/T10.8) provides detailed guidance on using GIS and ARC/INFO, the full-scale geographic information system used by the U.S. Environmental Protection Agency for hydrogeologic analysis.

²⁴ The geographic area that would exceed the capabilities of a stand-alone PC depends on two main factors: (1) the storage and memory capacity of the computer, and (2) the amount and number of layers of data that must be stored and processed. Most stand-alone PCs can readily handle a digitized USGS 7.5-min quadrangle map, which is adequate for most site-specific investigations. As the computational power of stand-alone PCs continues to increase, the distinction between full-scale and mini-GIS is likely to become more and more blurred.

²⁵ The cost of most commercial full-scale geographic information systems falls in the range of \$10,000 to \$100,000 (Rowe and Dulaney, 1991/T10.6). The cost of mini-GIS and related PC-based software ranges from hundreds to thousands of dollars.

²⁶ Baker, C.P., M.D. Bradley, and S.M. Kazco Bobiak. 1993. Wellhead Protection Area Delineation: Linking a Flow Model with GIS. *Journal of Water Resources Planning and Management (ASCE)* 119(2):275–287.

²⁷ Rifai, H.S., L.A. Hendricks, K. Kilborn, and P.B. Bedient. 1993. A Geographic Information System (GIS) User Interface for Delineating Wellhead Protection Areas. *Ground Water* 31(3):480–488.

²⁸ Brandon, F.O., P.B. Corcoran, and J.L. Yeo. 1992. Protection of Local Water Supplies by a Regional Water Supplier. *Ground Water Management* 13:525–538. [8th Focus Conference on Eastern GW Issues]

Table 10.5 Periodicals, Conferences, and Symposia with Papers Relevant to GIS

Sponsor	Year	Title
ACSM/ASPRS Annual Convention Proceedings		
	1986	Firm Foundations, New Horizons (Vol. 3, Geographic Information Systems, 286 pp.)
	1987	Technology for the Future, Applications for Today (7 vols.; Vol. 5, GIS/LIS, 222 pp.)
	1988	The World in Space (6 vols.; Vol. 5, GIS, 248 pp.)
	1989	Agenda for the Nineties (Vol. 4, GIS/LIS)
	1991	Annual Convention (6 vols.; Vol. 2, Cartography and GIS/LIS; Vol. 4, GIS)
	1992	Annual Convention (Vol. 1, ASPRS, 592 pp.; Vol. 2, ACSM, 283 pp.)
	1992	Global Change (5 vols.; Vol. 3, GIS and Cartography)
	1993	Annual Convention (Vol. 1, ACSM, 422 pp.; Vols. 2 and 3, ASPRS, 474 and 458 pp.)
Annual GIS Workshops/Conferences		
ASPRS/USFS	1986	Geographic Information Systems Workshop, 220 pp.
ACSM/ASPRS	1987	GIS'87: Into the Hands of the Decision Maker (2 vols., 760 pp.; Vol III, post conference proceedings, 234 pp.)
ACSM/ASPRS		
AAG/URISA	1988	GIS/LIS'88: Accessing the World (2 vols., 980 pp.)
	1989	GIS/LIS'89(2 vols., 980 pp.)
	1990	GIS/LIS'90 (2 vols., 960 pp.)
	1991	GIS/LIS'91 Proceedings (2 vols., 1045 pp.)
	1992	GIS/LIS'92 Proceedings (2 vols., 1355 pp.)
	1993	GIS/LIS'93 Proceedings (2 vols., 835 pp.)
	1994	GIS/LIS'94 Proceedings (2 vols., 880 pp.)
	1995	GIS/LIS'95 Proceedings
	1996	GIS/LIS'96 Proceedings (2 vols., 1285 pp.)
	1997	GIS/LIS'97 Proceedings (2 vols., 900 pp.)
	1998	GIS/LIS'98 Proceedings (CD Rom); last conference
Biannual International Automated Cartography Proceedings		
	1974	AutoCarto 1
	1987	AutoCarto 8 (775 pp.)
	1989	AutoCarto 9 (879 pp.)
	1991	AutoCarto 10 (Vol. 6 of ACSM/ASPRS Annual Convention Proceedings)
	1993	AutoCarto 11 (443 pp.)
	1995	AutoCarto 12
	1997	AutoCarto 13
Other Conferences/Symposia		
ASTM	1990	Geographic Information Systems (GIS) and Mapping: Practices and Standards
AWRA	1993	Geographic Information Systems and Water Resources
ASTM	1996	Remote Sensing and GIS for Site Characterization: Applications and Standards
Periodicals/Newsletters		
<u>Technical Journals:</u> Cartography and Geographic Information Systems (ACMS), GIS/GIMS News (ASPRS ^a), International Journal of GIS, Photogrammetric Engineering and Remote Sensing (ASPRS)		
<u>Vendor Newsletters:</u> ARC News (Environmental Systems Research Institute, Redlands CA ^a), Grass Clippings (Geographic Resource Analysis Support System, Stennie, Space Center, MS ^a), Monitor (Erdas, Inc., Atlanta, GA ^a), Remote Sensing and Database Development (James W. Sewall Company, Old Town, ME ^a), TYDAC News (TYDAC Technologies Corporation, Arlington, VA ^a)		
<u>Government Agency Newsletters:</u> Federal Geographic Data Committee (FDC) Newsletter (USGS, Reston, VA ^a), GIS News Layers (Division of Equalization and Assessment, Albany, NY ^a), GIS Update (Vermont Geographic Information System, Montpelier, VT ^a), MASS GIS Newsletter (Massachusetts GIS project, Boston ^a), New Jersey GIS Update (Department of Environmental Protection, Trenton, NJ ^a), NRGIS News (Minnesota Natural Resources Geographic Information Systems, St. Paul, MN ^a), RIGIS News (University of Rhode Island, Kingston, RI ^a)		

Table 10.5 Periodicals, Conferences, and Symposia with Papers Relevant to GIS (*Continued*)

Sponsor	Year	Title
<u>Other:</u> CAGIS Journal, Environmental Resources Research Institute Newsletter (Pennsylvania State University, University Park, PA ^a), Geo Info Systems, GIS Review (Greenland, NH ^a), GIS World (Fort Collins, CO ^a), Kansas Applied Remote Sensing (KARS) Newsletter (University of Kansas, Lawrence, KS ^a), The GIS Forum (Spring, TX ^a), SALIS Journal, URISA News (URISA, Washington, D.C. ^a), Wisconsin Land Information Newsletter (Center for Land Information Studies, University of Wisconsin, Madison, WI ^a)		

Note: AAG = Association of American Geographers; ACMS = American Congress on Surveying and Mapping; ASPRS = American Society for Photogrammetry and Remote Sensing; ASTM = American Society for Testing and Materials; AWRA = American Water Resources Association; UIRSA = Urban and Regional Information Systems Association.

* Addresses listed in August, P.V. and A. McCann. 1990. Geographic Information Systems (GIS) in Rhode Island. Department of Natural Resources Science Fact Sheet 90-23, University of Rhode Island, Kingston, RI, 11 pp.

Mini- and Desktop GIS. Mini-GIS performs most of the functions of full-scale GIS as an integrated software package that can be used with a stand-alone PC.²⁹ The specific capabilities of different commercial packages vary, but generally these systems include (1) a spatial database for geologic, hydrologic, and chemical data; (2) the ability to create base maps and special-purpose maps using data in the database; and (3) the ability to create geologic cross sections and graphs of time-series data. Often these systems can be used as preprocessors for numerical ground-water models (i.e., create grids and input values into the grid) and as postprocessors for graphic presentation of model output ([Section 10.5.2](#)).

PC-based software that performs more specific functions, such as graphic presentation of borehole logs, cross sections, and contour maps, can also facilitate the analysis of geologic and hydrologic data for hydrogeologic mapping.³⁰ Individual pieces of PC-based software that can handle spatial data can be used in combination to create a desktop GIS. Varljen and Wehrmann (1990)³¹ describe using AutoCAD® as a desktop GIS for a hydrogeological investigation. The base map contained digital data on terrain elevations, locations of transportation and water features, and names of cities, towns, and major landmarks in a CAD (computer-assisted drawing) DXF format (1:24,000 scale (7.5-ft quadrangles)). Additional layers containing hydrogeologic information were created using SURFER® and exported to AutoCAD for overlay on the base map.

The advantage of using mini-GIS software compared to using separate software to perform different functions is that import and export of data are minimized, reducing the time required for data processing. The advantage of desktop GIS, especially if one or more of the individual software packages have been purchased and are in use, is possibly lower cost and greater flexibility in processing and presenting data for the particular needs of the user.

Special Considerations in the Handling of Spatial Data. Spatial data are inherent to hydrogeologic mapping. For example, three coordinates are required to accurately locate borehole logging data: x and y coordinates define the position with respect to the surface of the earth, and the z coordinate defines the elevation. U.S. EPA and other federal agencies have adopted latitude and longitude as the standard system for x-y coordinates; new data collection should use that system. U.S. EPA (1992a, 1992b, 1992c/T10.8) provide guidance for collection of spatial data. Hydrogeologic data compiled from existing sources may be located using a variety of coordinate systems, such as *Township-Range-and-Section*, *state planar coordinates*, or *Universal Transverse Mercator* (UTM). If such data are to be processed electronically, conversion to a standard coordinate

²⁹ Examples of commercially available mini-GIS software packages include GEOBASE, SPASE, GIS\Key, StratiFact, and ROCKWORKS, described in Section 10.5.4.

³⁰ Examples of commercially available software that can create borehole and well construction logs include GTLog, logWRITER, QUICKLOG, and LOGGER. Software designed to create cross sections (also able to construct individual borehole logs) include GTGS, gINT, LOGGCORRELATE, and QUICKCROSS/FENCE. Available contouring software includes CONTUR, CoPlot, GRIDZO, LI-CONTOUR, PS-Plot, QUICKSURF, SURFER, TECKON, and TURBOCON.

³¹ Varljen, M.D. and H.A. Wehrmann. 1990. Using AutoCAD® as a Desktop GIS for Hydrogeological Investigations. In: Mapping and Geographic Information Systems, A.I. Johnson, C.B. Pettersson, and J.L. Fulton (eds.), ASTM STP 1126, American Society for Testing and Materials, Philadelphia.

system is required. Most mini-GIS software packages include conversion programs. The General Coordinate Transformation Package (GCTP) developed by the U.S. Geological Survey can be used to convert data between any of the commonly used geodetic coordinate systems (see address in Section 10.6).

10.5.6 Neural Networks and Automated Image Processing

Artificial neural networks, also called neuronets, are a relatively recently developed computer processing method where the pattern recognition capability of the brain is simulated by creating a weighted matrix through trial-and-error cycles. The weighted matrix can then be used to identify a given data pattern, classify objects, or estimate a dependent parameter. Basheer et al. (1996)³² used neural networks to map variations in soil permeability for the purpose of landfill siting. Mukhopadhyay (1999)³³ found that the method gave better estimates than the more commonly used geostatistical kriging method of spatial distribution of transmissivity of an aquifer in Kuwait.

A large number of digital image processing methods have been developed for analyzing binary and gray-scale images. These methods have been used for many years to assist in the interpretation of remote sensing imagery and geophysical measurements. More recently, these techniques have been used for stratigraphic and aquifer property characterization using CPT video cones (see Section 6.5.2).

10.6 GUIDE TO MAJOR INFORMATION SOURCES

The trend toward development of relatively inexpensive and user-friendly codes for ground-water modeling on personal computers increases the risk that pitfalls identified above will occur because users lack the required breadth of knowledge about hydrogeology and computer modeling. Short courses (usually focusing on a limited number of codes), such as those sponsored by the International Ground Water Modeling Center, the National Ground Water Association, and various universities, are the best way to gain hands-on experience with the use of more sophisticated models.

Table 10.6 provides an index to major text references and review papers on principles and applications of vadose zone and ground-water flow and contaminant modeling. Table 10.7 provides an index of major references documenting specific models. Mercer and Faust (1981) provide a good nontechnical introduction to ground-water modeling. Anderson and Woessner (1992) is a good source for advanced coverage of this topic.

The annual *Software Catalog* of the International Ground Water Modeling Center (see address below) contains over 50 PC-based ground-water programs that can be purchased for prices ranging from \$50 to \$1000. Ground-water flow and quality source codes developed by the U.S. Geological Survey can be obtained for IBM-compatible series 360 or 370 computers for \$40 per program from the U.S. Geological Survey, WRD, National Water Information System, 437 National Center, 12201 Sunrise Valley Drive, Reston, VA, 22092. Appel and Reilly (1988)³⁴ provide summary descriptions of these codes. Many commercially developed codes, including enhanced versions of public domain codes, such as MODFLOW, are available. Two good sources of commercially available software are Scientific Software Group and Rockware Scientific Software.³⁵

³² Basheer, I.A., L.N. Reddi, and Y.M. Najjar. 1996. Site Characterization by Neuronets: An Application to the Landfill Siting Problem. *Ground Water* 34:610–617.

³³ Mukhopadhyay, A. 1999. Spatial Estimation of Transmissivity Using Artificial Neural Network. *Ground Water* 37:458–464.

³⁴ Appel, C.A. and T.E. Reilly. 1988. Selected Reports That Include Computer Programs Produced by the U.S. Geological Survey for Simulation of Ground-Water Flow and Quality. *Water-Resources Investigations Report* 87-4271. [Provides summary information on about 40 models; March 6, 1991, update includes information on 16 more references]

³⁵ Rockware Scientific Software. *Earth Science & GIS Software Catalog*. Rockware Scientific Software, Golden, CO. [800-775-6745]. Scientific Software Group. *Environmental Software*. Scientific Software Group, Sandy UT. [866-620-9214]

The continuing enhancement of existing software and development of new codes make the task of keeping abreast with new developments a challenge. The following newsletters (available at no cost) are useful for this purpose:

IGWMC Ground Water Modeling Newsletter is published by the International Ground Water Modeling Center, Colorado School of Mines, Golden, CO, 80401-1887 (303-273-3103).

GeoTrans Newsletter often contains information on applications and recent developments in ground-water modeling (46050 Manekin Plaza, Sterling, VA 20166; 703-444-7000).

The scientific journals *Ground Water* and *Water Resources Research* are the best sources of peer-reviewed research on ground-water modeling. Periodic conferences sponsored jointly by IGWMC and other organizations are excellent sources of information on new developments and practical applications in ground-water modeling (NWWA/IGWMC, 1984, 1985, 1987, 1989; NGWA/IGWMC, 1992). [Table 10.6](#) identifies other conferences and symposia addressing ground-water modeling.

U.S. EPA's Center for Subsurface Modeling Support (CSMoS) provides ground-water and vadose zone modeling software and services to public agencies and private companies throughout the U.S. Its primary aim is to provide direct technical support to EPA and state decision makers and to coordinate the use of models for risk assessment, site characterization, remedial activities, wellhead protection, and GIS applications. [Table 10.7](#) identifies PC-based models that are available from CSMoS. The center's address is:

Center for Subsurface Modeling Support (CSMoS)
U.S. EPA R.S. Kerr Environmental Research Laboratory
P.O. Box 1198
Ada, OK 748201
580-436-8500
<www.epa.gov/ada/csmos.html>

Information on EPA exposure assessment modeling can be obtained from:

Center for Exposure Assessment Modeling (CEAM)
U.S. EPA Environmental Research Laboratory
960 College Station Road
Athens, GA 30605-2700
706-355-8400
<www.epa.gov/ceampubl/ceamhome.html>

[Table 10.8](#) provides an index of major references on GIS.

Table 10.6 Index to Major References on Ground Water and Vadose Zone Flow and Contaminant Transport Modeling

Topic	References
Ground Water Modeling (see ASTM (1999) for relevant standards)	
General ^a	<u>Texts</u> : Anderson and Woessner (1992), Bachmat et al. (1980), Bear and Bachmat (1990), Bear and Verruijt (1987), Boonstra and de Ridder (1981), Codell et al. (1982), Dagan (1989), Domenico (1972), Fried (1975), Javandel et al. (1984), Kinzelbach (1986), Mercer and Faust (1981), National Research Council (1990), Pinder and Gray (1977), Remson et al. (1971), van der Heijde et al. (1985), Walton (1988), Wang and Anderson (1982), Zienkiewicz (1977); <u>Computational/Mathematical Methods</u> : Boas (1983), Burden et al. (1981), Celia et al. (1988), Cross and Moscardini (1985), Gerald and Wheatley (1984), Hunt (1983), Huyakorn and Pinder (1983), Istok (1989), James et al. (1977), Kresick (1997), Liggett and Liu (1983), Press et al. (1986), Rushton and Redshaw (1979), Wood (1993); <u>Review Papers</u> : Anderson (1979), Bear et al. (1992), Faust and Mercer (1980), Faust et al. (1981), Gorelick (1983), Graves (1986), Konikow and Mercer (1988), Prickett (1979); <u>Quality Control</u> : Adrion et al. (1981), Buxton et al. (1989), California Toxic Substance Control Program (1990), Huyakorn et al. (1984), Kovar (1990), Moran and Mezgar (1982), Ross et al. (1982), U.S. EPA (1989), van der Heijde (1989), van der Heijde and Einawawy (1992), van der Heijde et al. (1989)
Conferences/Symposia	Arnold et al. (1982), Beck and Strateen (1983), Buxton et al. (1989), Celia et al. (1988), Custodio et al. (1988), Dickson et al. (1982), Haimes and Bear (1987), Jousma (1989), Kovar (1990), Melli and Zennetti (1992), NGWA/IGWMC (1992), NWWA/IGWMC (1984, 1985, 1987, 1989), Ritchey and Rumbaugh (1997), Wrobel and Brebbia (1991)
Reviews/Comparisons	Appel and Bredehoeft (1976), Appel and Reilly (1988), Arnold (1992), Bachmat et al. (1978), Beven (1989), Beljin (1988), El-Kadi et al. (1991), IMS/OSWER (1990), Kayser and Collins (1986), Kincaid and Morrey (1984), Kincaid et al. (1984), Mangold and Tsang (1987), Mercer et al. (1982), Morrey et al. (1986), van der Heijde and Beljin (1988), van der Heijde and Einawawy (1993), van der Heijde et al. (1988), Simmons and Cole (1985), Thompson et al. (1989), U.S. EPA (1988), Whelan and Brown (1988)
Applications	Anderson and Woessner (1992), Bachmat et al. (1978), Barnes and Rogers (1988), Boonstra and de Ridder (1981), Boutwell et al. (1985), Bredehoeft et al. (1982), Clark (1987), Haimes and Bear (1987), Holcomb Research Institute (1976), Kadi (1995), Keely (1987), Moskowitz et al. (1991), National Research Council (1990), OTA (1982), Pinder (2002 — with GIS), U.S. EPA (1988a, 1988b), van der Heijde and Beljin (1988), van der Heijde et al. (1985), Whelan and Brown (1988)
Selected Topics	<u>Analytic Element Method</u> : Haitjema (1995), Strack (1987); <u>Diffusion Models</u> : Choy and Reible (1999); <u>Stochastic Modeling</u> : Dagan (1989), El-Kadi (1984), Gelher (1993), Vomvoris and Gelhar (1986); <u>Modeling Contaminant Transport/Biodegradation</u> : Beljin (1988), Brusseau et al. (1993), Edwards and Smart (1988 — bibliography), Grant and Iskander (2000 — cold regions), Mueller and Crosby (1989 — comparison), Naymik (1987), Pinder (1984), Prickett et al. (1986), Travers and Sharp-Hansen (1993), Zheng and Bennett (2002); <u>Fracture Flow Modeling</u> : Schmelling and Ross (1989), van der Heijde and El-Kadi (1989), see also Table 7.6; <u>Multiphase Flow Modeling</u> : Abriola (1988), API (1982), Aziz and Settari (1979), El-Kadi et al. (1991), Guarnaccia et al. (1992), Mercer and Cohen (1990), Parker (1989)
Vadose Zone Modeling	
Overviews	Breckenridge et al. (1991), Donigian and Rao (1986a), El-Kadi and Beljin (1987), Ghadiri and Rose (1992), Hern and Melancon (1986a), Iskander (1981), Mackay (2001), Mangold and Tsang (1987), National Research Council (2001 — fractured), Nielsen et al. (1990), Nofiziger et al. (1994), Oster (1982), Thompson et al. (1989), U.S. EPA (1984, 1988a, 1988b), van der Heijde (1994), van Genuchten (1987), Weaver et al. (1989), Whelan and Brown (1988), Wierenga (1991); <u>Hydrocarbon Fate</u> : Bonazountas (1991), Bonazountas and Kallidromitou (1993)
Conference/Symposia	Arnold et al. (1982), Beasley et al. (1991), Evans and Nicholson (1987 — fractured rock), Ritchey and Rumbaugh (1997), Wierenga and Bachelet (1988)
Model Comparisons	Addiscott and Wagenet (1985), Donigian and Rao (1986b), Kincaid and Morrey (1984), Kincaid et al. (1984), Oster (1982), van der Heijde et al. (1988)

Table 10.6 Index to Major References on Ground Water and Vadose Zone Flow and Contaminant Transport Modeling (*Continued*)

Topic	References
Field Testing	Hern and Melancon (1986b), Hern et al. (1986), van der Heijde et al. (1989), Weaver et al. (1989)
Hydrogeochemical Modeling	
General	Apps (1988), Boulding (1990), Jacobs and Whatley (1985), Jenne (1979, 1981), Logan (2001), Melchior and Bassett (1990), NWWA (1988, 1990), Siegel and Leigh (1985), U.S. EPA (1990), Yeh and Tripathi (1989)
Model Comparisons	Mangold and Tsang (1987), Nordstrom and Ball (1984), Nordstrom et al. (1979), Rice (1986), Schechter et al. (1985), Sposito (1985)
Risk Assessment Modeling (see Table 11.10)	

^a Most ground-water and hydraulics texts in Table 2.4 cover governing analytical equations.

Table 10.6 References (Appendix F contains references for figure and table sources.)

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* The International Ground Water Modeling Center is now located in Golden, Colorado. Prices subject to change.

** See Preface for information on how to obtain documents from CERL and NTIS.

Table 10.7 Index to References on PC-Based Ground Water and Vadose Zone Flow and Contaminant Transport Models^a

Topic	References
Ground Water Flow	Aral (1990a — SLAM, 1990b — ULAM), Bair et al. (1991 — CAPZONE), Blandford and Huyakorn (1991 — WHPA), Bonn and Rounds (1990 — DREAM), Franz and Guiguer (1990 — FLOWPATH), McDonald and Harbaugh (1988 — MODFLOW), Pollack (1988 — MODPATH), Prickett and Associates (1984 — PLASM), Prickett and Lonquist (1971 — PLASM), Shafer (1987, 1990), Trescott (1975 — USGS-3D-FLOW), Trescott et al. (1976 — USGS-2D), U.S. EPA (1993 — MODFLOW), van der Heijde (1987 — THWELLS), Walton (1989a — PLASM, 1989b — WELFLO, 1992 — MODFLOW, MODPATH), WellWare (1993 — Ressq), Zheng (1992b — PATH3D), Zheng et al. (1992 — PATH3D); <u>Analytic Element Models</u> : Haitjema et al. (1994 — WhAEM), Strack et al. (1994 — CZAEM); <u>Analytical Models</u> : Cleary and Ungs (1978), Walton (1962, 1984a, 1984b — WALTON35)
Solute Transport/Biodegradation	Bedient et al. (1989 — BIOPLUMEII), Domenico and Palciauskas (1982 — VHS), Freeze et al. (1992), Hostetler et al. (1988 — FOWL), Konikow and Bredehoeft (1978 — MOC), Newell et al. (1990), Park et al. (1992 — VIRALT), Prickett and Associates (1984 — Random Walk), Rifai et al. (1988 — BIOPLUMEII), Strack (1989 — SLAEM), Summers et al. (1989 — MYGRT), U.S. EPA (1985 — EPA-VHS), Walton (1989a — Random Walk, 1989b — CONMIG, 1992 — MOC, SUTRA), Watershed Research (1988 — Hydropal Slug), Yeh (1981 — AT123D), Zheng (1990, 1992a — MT3D); <u>Analytical Solutions/Nomographs</u> : Dragun (1989 — CDT nomograph), Galya (1987), Guswa et al. (1987 — rapid assessment nomograph), Kent et al. (1982 — Wilson–Miller nomograph), van Genuchten and Alves (1982)
Hydrogeochemical	Ball and Nordstrom (1991 — WATEQ4F), Brown and Allison (1987 — MINTEQA1), Parkhurst et al. (1980 — PHREEQE)
Vadose Zone	<u>Hydrologic</u> : Perrier and Gibson (1984 — HSSWDS), Ross (1990 — SWIM), Schroeder et al. (1984a, 1984b — HELP), van Genuchten et al. (1991 — RETC), Walton (1992 — INTERSAT); <u>Fate and Transport</u> : Bonazountas and Wagner (1984 — SESOIL), Brown and Boutwell (1988 — POSSM), Carsel et al. (1984 — PRZM), CH2M Hill (1990 — VLEACH), Davis et al. (1990 — GLEAMS), Dean et al. (1989 — RUSTIC), General Sciences Corporation (1989 — PCGEMS/SESOIL), Knisel (1980 — CREAMS), McCone et al. (1987 — Geotox), Nofziger and Hornsby (1987 — CMLS), Nofziger and Williams (1988 — RITZ), Nofziger et al. (1989 — CHEMFLO), Pennsylvania Bureau of Waste Management (1989 — RAFT), Shields et al. (1987 — MCPOSSM), Sims et al. (1991 — STF/RITZ/VIP), Stevens et al. (1993 — VIP), Varadhan and Johnson (1992 — PESTAN), Walton (1992 — INTERTRANS); <u>Soil Vapor</u> : Johnson (1992 — HyperVentilate), Kruger and Morse (1992 — HyperVentilate)
Water Budget	<u>Precipitation–Runoff</u> : Leavesly et al. (1983)
EPA Software	
Ground-Water Models	See references above for following models: BIOPLUMEII, EPA-VHS, MT3D, OASIS, WhAEM/CZAEM, WHPA; <u>Hydrogeochemical</u> : MINTEQA1
Vadose Zone Models	See references above for following models: CHEMFLO, HELP, HSSWDS, HyperVentilate, PCGEMS/SESOIL, PESTAN, PRZM, RETC, RITZ, RUSTIC, SESOIL, STF, VIP, VLEACH
Statistics	<u>Conventional</u> : Lin (1986, 1993); <u>Geostatistics</u> : England and Sparks (1988, 1991), Yates and Yates (1990); <u>Ground Water</u> : U.S. EPA (1992 — GRITS/STAT) <u>Uncertainty Analysis</u> : Klee (1990, 1992); <u>QA/QC</u> : Johnson et al. (1987 — PC-QTRAK), Simon et al. (1991 — CADRE), U.S. EPA (1991a — ASSESS), van Ee et al. (1990)
Other	Kollig et al. (1991 — FATE), U.S. EPA (1991b); <u>MULTIMED</u> : Salhotra et al. (1993), Sharp-Hansen et al. (1992)
Other Statistical Software	
Geostatistics	Deutsch and Journal (1993 — GSLIB)

Table 10.7 Index to References on PC-Based Ground Water and Vadose Zone Flow and Contaminant Transport Models^a (Continued)

Topic	References
Commercial Software Vendors	
See above for references	<u>Charles R. Fitts</u> : TWODAN; <u>GeoTrans</u> : SEFTRAN, SWAN-FLOW, MOD3D (MODFLOW), BIO1D, FRACFLOW; <u>Geraghty and Miller</u> : AQTESOLV, ModelCad, MODFLOW, MODPATH, MOC, SUTRA, QuickFlow; <u>S.S. Papadopoulos and Associates</u> : MT3D, PATH3D; <u>Prickett and Associates</u> : PLASM, Random Walk; <u>Strack Consulting</u> : SLAEM; <u>Waterloo Hydrogeologic Software</u> : AIRFLOW, FLONET, FLOWPATH; <u>Water-Shed Research</u> : Hydropal; <u>WellWare</u> : AqModel, RessqM

^a See IGWMC (2001) for available models and footnote 35 for information on how to obtain current catalogs from Rockware and Scientific Software Group.

Table 10.7 References

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Table 10.8 Index to Major References on GIS

Topic	References
Texts	Deliska (2002 — dictionary), Green et al. (1993), Lo (2002), Luarini and Thompson (1992), Warboys (1994); <u>Introductory</u> : Aronoff (1989), Bernhardson (2002), Cadoux-Hudson and Heywood (1992), Chang (2002), Heywood (2002), Pequet and Marble (1990), Ripple (1989), Star and Estes (1990); <u>Cartography</u> : ACSM (1992d), Clarke (1990), Johnson et al. (1992), Tomlin (1990); <u>Technology</u> : ACSM (1992b), Antenucci et al. (1991), Maguire et al. (1992); <u>Land Resource Assessment</u> : Burrough (1986), Gokee and Joyce (1992), McCloy (1994), Ripple (1986), Young and Cousins (1993); <u>Urban Applications</u> : Huxhold (1991); <u>Geoscience/Geotechnical Applications</u> : Johnson et al. (1992), Thomas (1988); <u>Ground-Water and Environmental Applications</u> : Clark (2002), Douglas (1994), Goodchild et al. (1993), Halls (2001), Johnson et al. (1992), Kovar and Nachtnebel (1993), Lyon and McCarthy (1995), Maidment and Djokic (2000), Pickus (1992), Singhroy et al. (1996), Skidmore (2002), Vieux (2001); <u>General Applications</u> : Johnson et al. (1992), Maguire et al. (1991), Ripple (1986); <u>Temporal GIS</u> : Egenhofer and Golledge (1998), Langran (1992), Ott (2001)
GIS Systems	<u>Online</u> : Bossmailer (2002); <u>Arc/Info</u> : ESRI (1990a, 1990b), Pickus (1992); <u>AutoCAD</u> : Jones and Martin (1988); <u>TIGER</u> : Bureau of Census (1992); <u>Comparison/Evaluation</u> : FICC (1988), Rowe and Dulaney (1991)
Government Use	<u>U.S. EPA</u> : Hewitt et al. (1993), OIRM (1992), U.S. EPA (1992a, 1992c, 1992d); <u>U.S. Geological Survey</u> : USGS (1991a); <u>Soil Conservation Service</u> : SCS (1991); <u>Other Federal</u> : FGDC (1991a, 1991b, 1993), FICC (1990); <u>States</u> : ACSM (1992a), August and McCann (1990), PlanGraphics (1991), Warnecke et al. (1992); <u>Local</u> : ACSM (1992c)
Spatial Data	<u>Analysis</u> : Fotheringham and Rogerson (1994), Goodchild and Gopal (1989), Raper (1989), Samet (1990), Tomlin (1990), Turner (1991), Unwin (2002), Zhang (2002); <u>Data Management/Processing</u> : Bossler (2002), Date (1985, 1990), Ferigno (1986), Fleming and von Halle (1986), Green (1985), International Geographical Union Commission on GIS (1992), Lin and Harbaugh (1984), Michener et al. (1994), Samet (1989, 1990), Shi (2002); <u>Standards/Format</u> : Elissal and Caruso (1983), Johnson et al. (1992), National Committee for Cartographic Data Standards (1987), USFWS (1984), USGS (1990a, 1990b, 1991b); <u>Information Exchange</u> : ANSI (1986a, 1986b), Bureau of Census (1992 — TIGER), Moellerling (1991), Morrison and Wortman (1992), NIST (1992), USGS (1992); <u>Data Coding</u> : NBS (1987, 1988), U.S. EPA (1992d), USGS (1983); <u>Locational Methods/Surveying</u> : Onsrud and Cook (1990), U.S. EPA (1992a, 1992b, 1992c); <u>Data Sources</u> : See Table 5.13

Table 10.8 References (Appendix F contains references for figure and table sources.)

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* See Preface for information on how to obtain documents from CERL and NTIS.

PART III

Prevention and Remediation

Prevention and Minimization of Contamination

11.1 GENERAL APPROACHES

The two major approaches to prevention or minimization of contamination of soil and ground water are waste management and control at specific facilities (Section 11.1.1) and delineation and management of wellhead protection areas (Section 11.1.2). Section 11.1.3 provides a brief overview of other approaches.

11.1.1 Facility-Specific Waste Management and Control

Waste minimization and pollution prevention make both economic and environmental sense and have received increasing emphasis in environmental programs in recent years.¹ Techniques for waste minimization fall into two major categories: (1) source reduction and (2) recycling. The discussion here focuses on waste minimization in the industrial and commercial sector, but the basic approaches can be applied to waste minimization for any activity.

Source Reduction. Source reduction can be achieved by *product changes*, such as product substitution, product conservation, and changes in product composition, and *source control*. Source control can be achieved by various methods:

- *Input material changes*, such as material purification and material substitution
- *Technology changes*, such as modifications of process, equipment, piping or layout, additional automation, and changes in operational settings
- *Good operating practices*, including procedural measures for loss prevention, management practices, waste stream segregation, and improved material handling and production scheduling

Recycling. Recycling can take place both on-site and off-site and can be accomplished by *reuse* (either by returning to the original process or use as a raw material substitute for another process) or *reclamation*, where spent materials are processed for resource recovery or processed as a by-product.

Life Cycle Analysis. Waste minimization is most effectively accomplished by life cycle analysis, which provides a complete environmental profile of goods and services. The life cycle consists of each step from the acquisition of raw materials through processing, manufacture, use, and final disposal of all residuals. Source reduction is most easily accomplished using the life cycle design

¹ The term *pollution prevention* has a broader connotation that includes waste minimization, and waste treatment and controlled disposal. However, it may also be used interchangeably with waste minimization. For example, EPA's series of guides to pollution prevention (discussed later in this section) actually focus on waste minimization as described in the rest of this section.

approach for new facilities, but there may also be significant opportunities for source reduction by product changes at existing facilities.

A number of good documents are available from the U.S. EPA for assessing opportunities for waste minimization and pollution prevention: (1) *Waste Minimization Opportunity Assessment Manual* (U.S. EPA, 1988e/T11.11), and (2) *Facility Pollution Prevention Guide* (U.S. EPA, 1992d/T11.11). EPA's *Life Cycle Design Guidance Manual* (U.S. EPA, 1993b/T11.11) provides up-to-date guidance on use of life cycle analysis to meet environmental objectives.

A number of ongoing publications series by the U.S. EPA are useful for identifying opportunities for waste minimization in specific manufacturing, commercial, and other activities (all available from EPA's Center for Environmental Research Information, while supplies last). These include the *Guides to Pollution Prevention* (U.S. EPA, 1990–1993/T11.11), *Waste Minimization Assessments* (U.S. EPA, 1990–1992/T11.11), and *Waste Reduction Activities and Opportunities* (U.S. EPA, 1992f/T11.11). There are more than 70 specific activities consolidated in the citations for the three series, and all three should be reviewed if more detailed information about a particular activity is desired. [Table 11.11](#) also provides an index to a number of other major references on waste minimization and pollution prevention in industrial and commercial activities.

11.1.2 Wellhead Protection Area Management

The 1986 Amendments to the Safe Drinking Water Act (SDWA) established the Wellhead Protection Program (WHP), which required states to develop a WHP to protect drinking water supplies as part of a Comprehensive State Ground-Water Protection Program. The wellhead protection area (WHPA) is the primary unit in this program, and most of the rest of this chapter focuses on the process of delineating WHPAs ([Section 11.2](#)), identifying potential contaminant sources ([Section 11.3](#)), assessing their risk ([Section 11.4](#)), and developing WHPA management strategies to prevent contamination ([Section 11.5](#)).

11.1.3 Other Approaches and Programs

Section 11.5 identifies numerous specific approaches to prevention of soil and ground-water contamination. Various federal and state regulatory programs, developed pursuant to legislation such as the Clean Water Act of 1972, Safe Drinking Water Act of 1974, Toxic Substances Control Act of 1976, Resource Conservation and Recovery Act of 1976 (and subsequent amendments to each act), have as a primary or secondary focus prevention or minimization of soil and ground-water contamination. In addition to the Wellhead Protection Program, the Underground Injection Control (UIC) and Sole Source Aquifer (SSA) programs developed pursuant to the Safe Drinking Water Act focus on ground-water protection. The UIC program regulates injection of fluids into five classes of wells with the primary focus of ensuring that underground drinking water sources are not contaminated. The SSA program permits EPA to designate aquifers that are the sole or principal drinking water sources for an area and that, if contaminated, would present a significant hazard to human health. The main protection afforded by sole source aquifer designation is the withholding of federal financial assistance for any project that may contaminate the aquifer or create a significant public health hazard. [Table 11.11](#) provides an index to major references on federal and state ground-water protection programs.

11.2 DELINEATION OF WELLHEAD PROTECTION AREAS

11.2.1 Criteria for Delineation of Wellhead Protection Areas

U.S. EPA (1987a/T11.11) defined five criteria that may be used singly or in combination to define the area around a well in which contamination could represent a threat to drinking water

Table 11.1 Comparison of Major Methods for Delineating Wellhead Protection Areas

Methods/Criteria	Advantages	Disadvantages
Geometric Methods		
Arbitrary fixed radius (distance)	<ul style="list-style-type: none"> • Easily implemented • Inexpensive • Requires minimal technical expertise 	<ul style="list-style-type: none"> • Low hydrogeologic precision • Large threshold radius required to compensate for uncertainty will generally result in overprotection • Highly vulnerable aquifers may be underprotected • Highly susceptible to legal challenge
Cylinder method (calculated fixed radius)	<ul style="list-style-type: none"> • Easy to use • Relatively inexpensive • Requires limited technical expertise • Based on simple hydrogeologic principles • Only aquifer parameter required is porosity • Less susceptible to legal challenge 	<ul style="list-style-type: none"> • Tends to overprotect downgradient and underprotect upgradient because it does not account for ZOC • Inaccurate in heterogeneous and anisotropic aquifers • Not appropriate for sloping potentiometric surface or unconfined aquifer
Simplified variable shapes (TOT, flow boundaries)	<ul style="list-style-type: none"> • Easily implemented once shapes of standardized forms are calculated • Limited field data required once standardized forms are developed (pumping rate, aquifer material type, and direction of ground-water flow) • Relatively little technical expertise required for actual delineation • Greater accuracy than calculated fixed radius for only modest added cost 	<ul style="list-style-type: none"> • Relatively extensive data on aquifer parameters required to develop the standardized forms for a particular area • Inaccurate in heterogeneous and anisotropic aquifers
Other Methods		
Simple analytical methods (TOT, drawdown, flow boundaries)	<ul style="list-style-type: none"> • More accurate than simplified variable shapes because based on site-specific parameters • Technical expertise required, but equations are generally easily understood by most hydrogeologists and civil engineers • Various equations have been developed, allowing selection of solution that fits local conditions • Allows accurate characterization of drawdown in the area closest to a pumping well • Cost of developing site-specific data can be high 	<ul style="list-style-type: none"> • Relatively extensive data on aquifer parameters required for input to analytical equations • Most analytical models do not take into account hydrologic boundaries, aquifer heterogeneities, and local recharge effects
Hydrogeologic mapping (flow boundaries)	<ul style="list-style-type: none"> • Well suited for unconfined aquifers in unconsolidated formations and to highly anisotropic aquifers such as fracture bedrock and conduit-flow karst • Necessary to define aquifer boundary conditions 	<ul style="list-style-type: none"> • Less suitable for deep, confined aquifers • Requires special expertise in geomorphic and geologic mapping and judgment in hydrogeologic interpretations • Moderate to high manpower and data collection costs

Table 11.1 Comparison of Major Methods for Delineating Wellhead Protection Areas (Continued)

Methods/Criteria	Advantages	Disadvantages
Computer semianalytical and numerical flow/transport models (TOT, drawdown, flow boundaries)	<ul style="list-style-type: none">• Most accurate of all methods and can be used for most complex hydrogeologic settings, except where karst conduit flow dominates• Allows assessment of natural and human-related affects on the ground water system for evaluating management options	<ul style="list-style-type: none">• High degree of hydrogeologic and modeling expertise required• Less suitable than analytical methods for assessing drawdowns close to pumping wells• Extensive aquifer-specific data required• Most expensive methods in terms of manpower and data collection/analysis costs

Source: Boulding (1994).

drawn from the well: (1) distance, (2) drawdown, (3) time of travel, (4) flow boundaries, and (5) assimilative capacity. These are described briefly below.

Distance. The distance criterion uses a fixed radius or other dimension from a well to delineate a WHPA. This criterion usually is based on some kind of analysis involving the application of other criteria to generalized hydrogeologic settings. The approach is simple and very inexpensive. It is only suitable as a preliminary step, because the criterion considers ground-water flow or contaminant processes only indirectly. Since the zone of contribution (discussed below) rarely is circular, a fixed radius that provides adequate protection will almost always include areas for which protective actions are not required. Distance is also the *end product* of the application of other delineation criteria.

Drawdown. Drawdown occurs when water is removed from an aquifer by pumping. The water level declines in the vicinity of the well, creating a gradient that drives water toward the discharge point. The gradient becomes steeper closer to the well, because the flow is converging from all directions and the area through which the water flows gets smaller. This results in a *cone of depression* around the well (Figure 2.17). The cone of depression around a well tapping an unconfined aquifer is relatively small compared to that around a well in a confined system. The former may be a few tens to a few hundred feet in diameter, while the latter may extend outward for miles.

The *zone of influence* (ZOI) is the distance from the well where changes in the ground-water surface can be measured or inferred as a result of pumping (Figure 11.1). In a homogenous, porous aquifer, the ZOI will be circular. In heterogenous porous and fractures aquifers, the ZOI typically has an elliptical or irregular shape. Ground-water velocities increase within the cone of depression of a well, causing contaminants to flow more rapidly toward the well. The drawdown criterion accurately defines areas requiring protection over the aquifer downgradient from the well, but generally does *not* include the zone of contribution upgradient based on flow boundaries (Figure 11.1).

Time of Travel (TOT). The time-of-travel criterion requires delineation of *isochrones* (contours of equal time) on a map that indicate how long water or a contaminant will take to reach a well from a point within the zone of contribution. The WHPA falls in the portion of the zone of contribution that is downgradient from the selected isochrone (say 50 years time of travel). This area is called the *zone of transport* (ZOT). When the zone of contribution to a well is large (i.e., ground water from the farthest parts may take hundreds or thousands of years to reach the well), the ZOT will define a smaller area than the ZOC criterion (Figure 11.1). If the ZOC is small, the two will generally overlap.

Flow Boundaries (Zone of Contribution). The flow boundary criterion uses mapping of ground water divides and other physical and hydrologic features that control ground-water flow to define the geographic area containing ground water that flows toward a pumping well (Figure 11.1). Designating this *zone of contribution* (ZOC) as the WHPA provides the maximum amount of protection, although there are special cases where the drawdown (zone of influence) and time-of-travel (zone of transport) criteria will coincide with the ZOC.

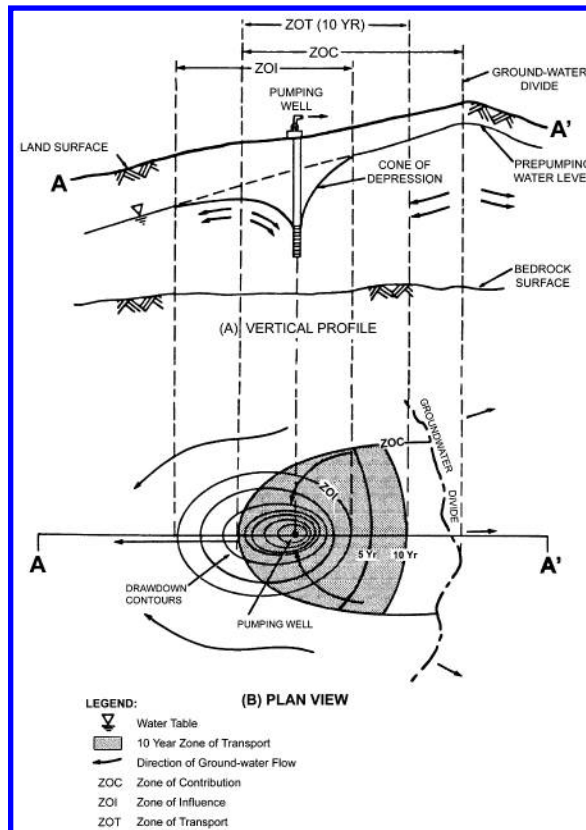


Figure 11.1 Relationship between ZOI, ZOT, and ZOC in an unconfined aquifer with a sloping regional water table (U.S. EPA, 1987b).

Assimilative Capacity. The assimilative capacity criterion allows the reduction of a WHPA if contaminants are immobilized or attenuated while moving through the vadose zone of the aquifer so that concentrations are within acceptable limits by the time they reach a pumping well. This may occur by processes of dilution, dispersion, sorption, chemical precipitation, and biological degradation. A WHPA defined by this criterion would include the *zone of attenuation* (ZOA).

This criterion can be used in several ways. Incorporation of an empirical *retardation factor* for a specific contaminant that represents the combined effects of attenuation processes in the aquifer into time-of-travel calculations would result in a shift of isochrones closer to the well. A more complex application involves establishing an acceptable concentration of a contaminant at the well and using solute transport models to define the distance required to avoid exceeding the target concentration.

In practice, this is an unrealistic approach because of the difficulty of characterizing aquifer physical and chemical properties for transport modeling of multiple contaminants. Where only one or two contaminants, such as nitrate loadings from septic tanks or pesticide loadings, are of primary concern, this approach may be very useful.

11.2.2 Overview of Wellhead Protection Delineation Methods

Classification of Delineation Methods. Because the process of wellhead delineation typically involves the use of more than one of the criteria discussed in the previous section, methods for wellhead delineation are not readily classified into distinctive categories. This guide classifies WHPA delineation methods into four major groups of generally increasing complexity:

1. *Geometric* methods involve the use of a predetermined fixed radius and aquifer geometry without any special consideration of the flow system (such as the cylinder method shown in Figure 11.2), or the use of simplified shapes that have been precalculated for a range of pumping and aquifer conditions (Figure 11.3).
2. *Simple analytical* methods allow calculation of distances for wellhead protection using equations that can be solved using a hand calculator or microcomputer spreadsheet program. These methods fall into two major groups, which are often used in combination: (1) time-of-travel calculations (Section 2.6.5), and (2) drawdown calculations, using aquifer test analytical equations that are rearranged to solve for distance to a specific drawdown criterion using measured or estimated values for other aquifer parameters.
3. *Hydrogeologic mapping* involves identification of the zone of contribution (as defined by flow boundaries) based on geomorphic, geologic, hydrologic, and hydrochemical characteristics of an aquifer. This is often used in combination with simple analytical methods and is usually required when using more complex analytical and numerical computer flow and transport models. Section 7.5 addresses special considerations in hydrogeologic mapping.
4. *Computer modeling* methods involve the use of more complex analytical or numerical solutions to ground-water flow and contaminant transport processes. Chapter 10 covers ground-water flow modeling in more detail.

This classification scheme is generally similar to that used in U.S. EPA (1987a/T11.11), with the following differences: (1) the arbitrary fixed-radius, volumetric flow equation (Figure 11.2), and simplified shapes methods (Figure 11.3) are all placed in the geometric category; (2) the calculated fixed radius is dropped as a category because the two examples given fall into separate categories (the volumetric equation is geometric, and the Vermont Department of Water Resources method is a simple analytical method using a drawdown criterion); and (3) the numerical flow/transport models category includes more complex analytical models that require computer programs for solution.

Table 11.1 summarizes the advantages and disadvantages and identifies the type of threshold criteria used for the three geometric methods and the three other major types of methods for

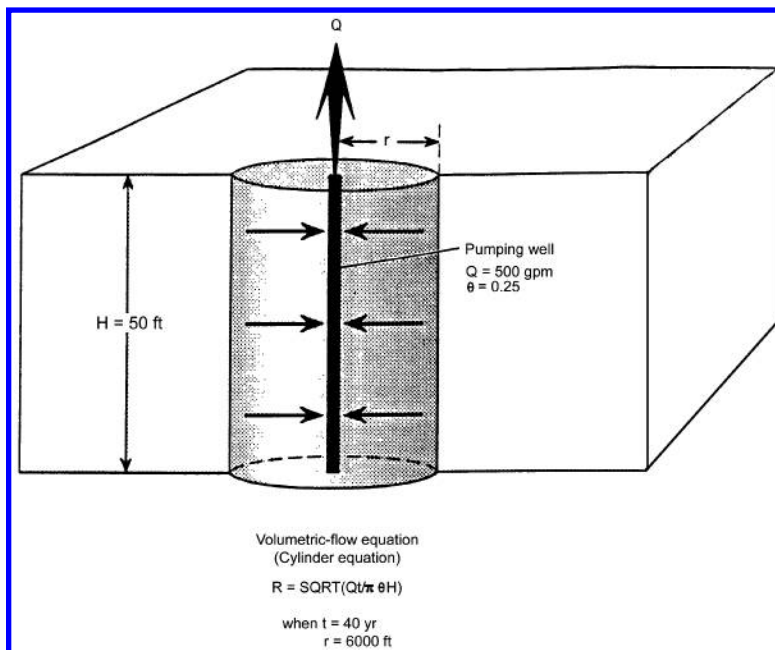


Figure 11.2 WHPA delineation using cylinder method (Kreitler and Senger, 1991).

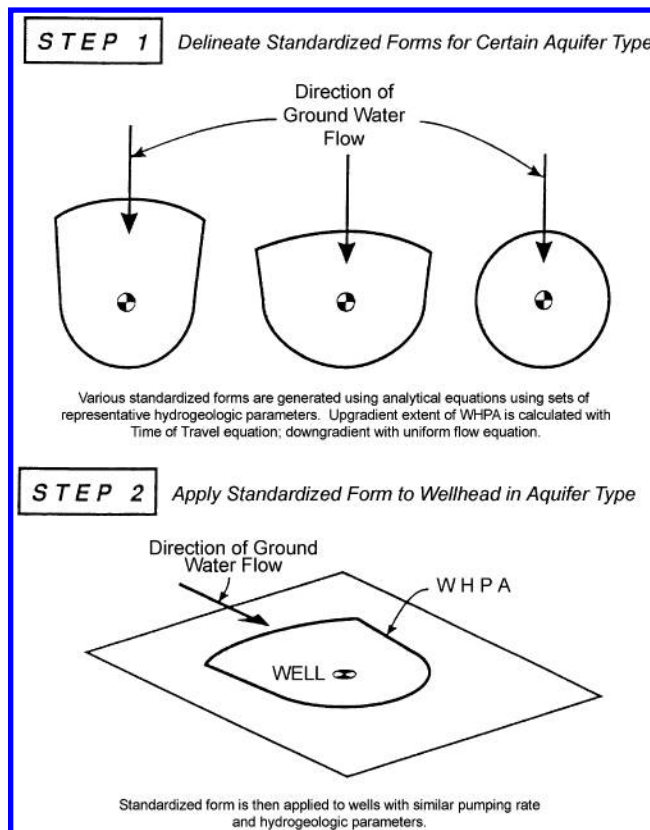


Figure 11.3 WHPA delineation using simplified shapes method (U.S. EPA, 1993).

delineating WHPAs (simple analytical methods, hydrogeologic mapping, and computer modeling). Important references focusing on special geologic settings for WHPA delineation include Kreitler and Senger (1991/T11.11) for confined aquifers and Bradbury et al. (1991/T11.11) for fractured rock aquifers. All state submittals to the U.S. Environmental Protection Agency for approval of wellhead protection programs contain a section describing WHPA delineation methods to be used in the state. Often these documents contain state-specific criteria for the application of geometric methods ([Section 11.2.4](#)).

Relationship of Protection Areas Based on Different Criteria. [Table 11.2](#) provides summary definitions of types of wellhead areas based on four of the five criteria for wellhead protection: (1) zone of influence (ZOI); (2) zone of travel (ZOT); (3) zone of contribution (ZOC); and (4) zone of attenuation (ZOA). The first criterion, a fixed-distance threshold, is based on a qualitative or semiquantitative application of one or more of these criteria. [Table 11.2](#) also defines the hydrogeologic or other conditions required for one zone to be less than, equal to, or greater than another zone, and provides an indication of how commonly the relationship occurs. In general, the following relationships occur: $ZOA < ZOI < ZOT < ZOC$.

11.2.3 Vulnerability Mapping

Ground-water vulnerability mapping involves the delineation of areas of varying susceptibility to ground-water contamination based on the interaction of characteristics that promote or inhibit movement of contaminants in the subsurface. Ground-water vulnerability maps may be developed

Table 11.2 Relationships of WHPAs Based on ZOI, TOT, ZOT, ZOC, and ZOA

Terms/Relationship	Description
Zone of influence	ZOI = area of drawdown or the cone of depression around a well created by pumping
Zone of travel ^a	ZOT = area around a well defined by a time-of-travel (TOT) isochrone and aquifer boundaries; ZOT _{max} = ZOT defined by TOT _{min} isochrone or the edge of the ZOC, whichever is closer to the well
Zone of contribution	ZOC = portion of an aquifer in which all recharge and ground water flows toward a pumping well; the boundaries of the ZOC are defined by ground water divides and other aquifer boundaries
Zone of attenuation	ZOA = area around an aquifer capable of reducing concentrations of a contaminant entering the area at a specified maximum concentration level to less than a defined acceptable concentration at the well
ZOI < ZOT	When distance to TOT _{min} isochrone (i.e., ZOT _{max} boundary edge) lies outside the cone of depression; most common situation for unconfined aquifers
ZOI = ZOT	When distance to TOT _{min} isochrone = distance to ZOI boundary edge
ZOI > ZOT	When TOT _{min} isochrone lies within cone of depression for a well; unlikely to occur in unconfined aquifers; may occur in confined aquifers with very large ZOI
ZOI < ZOC	When upgradient ground water divide lies outside cone of depression; the case in most hydrogeologic settings
ZOI = ZOC	Rare; may occur with flat water table, with high recharge from rainfall within ZOI; also possible when ZOI straddles a ground water divide
ZOI > ZOC	Cannot occur
ZOT < ZOC	When distance to TOT _{min} isochrone < distance to ZOC boundary; the most common situation; the difference between the two zones decreases as the TOT threshold criterion increases
ZOT = ZOC	When distance to TOT _{min} isochrone = distance to ZOC boundary
ZOT > ZOC	By definition, cannot occur; however, in this situation TOT is less than TOT _{min} , indicating that the well is very vulnerable to contamination from sources within the ZOC
ZOA < ZOT	When assimilative capacity is >0
ZOA = ZOT	When contaminant is not attenuated by the aquifer

Note: TOT = time of travel for ground water or contaminants from a point in an aquifer to a pumping well; TOT_{min} = the minimum acceptable time of travel for purposes of wellhead delineation; TOT isochrone = a line from which TOT is the same at all points to a pumping well.

^a Defined by time-of-travel criterion.

Source: Boulding (1994).

as specific units within a broader scheme of ground-water classification, or may just delineate highly vulnerable areas without paying special attention to the characteristics of nonvulnerable areas.

Figure 11.4 illustrates WHPAs based on an arbitrary radius and simplified shape marked on a vulnerability map of Door County, Wisconsin. When vulnerability mapping is performed, efforts to inventory potential contaminant sources can be focused on areas where the hazard is greatest. Vulnerability mapping also allows fine-tuning of management approaches within the WHPA. Highly vulnerable areas require stricter management approaches than less vulnerable areas. The rest of this section reviews a number of approaches that have been developed for vulnerability mapping.

DRASTIC. DRASTIC is a widely used method for evaluating the relative vulnerability of mappable hydrogeologic units to ground-water contamination. DRASTIC is an acronym for the seven factors for which numerical ratings are made to develop an index of vulnerability to ground water contamination: *d*epth to water table, *n*et *r*echarge, *a*quifer media, *s*oil media, *t*opography (slope), *i*mpact to vadose zone, and hydraulic *c*onductivity of the aquifer. Conventional hydrogeologic mapping methods are first used to delineate areas with similar characteristics. A numerical value is given to each of the seven factors, which are multiplied by a weighting factor and added for the DRASTIC index for the map unit. Worksheet D-W6 provides a form for calculating the DRASTIC index.

The DRASTIC index does not have any absolute meaning, but provides a means to assess relative vulnerability. A DRASTIC index of greater than 150 is one means of defining a highly vulnerable aquifer under EPA's ground-water protection strategy (U.S. EPA, 1986a/T11.10). The

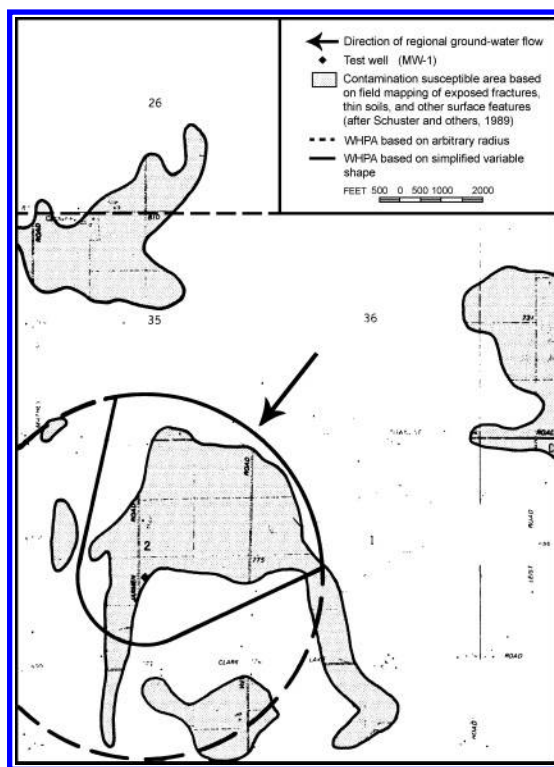


Figure 11.4 WHPAs at Sevastopol site, Door County, WI, based on fixed radius, simplified shape, and vulnerability mapping (Bradbury et al., 1991).

DRASTIC index has been found to give inconsistent results in karst areas where the water table is relatively deep (Sendlein, 1992/T11.10), and in the arid Tucson basin, Arizona, for reasons that are not entirely clear (Pima Association of Governments, 1992/T11.10). Both of these studies suggest that the relatively high weighting given to depth to water may understate the potential for contamination when preferential pathways allow relatively rapid vertical migration to deep water tables. Another weakness in the DRASTIC index is that it does not readily allow differentiation of shallow perched water tables over deeper regional water tables.

Other Vulnerability Mapping Methods. Various other methods have been developed for vulnerability mapping. They can be broadly classified as (1) systems using numerical ratings (as with DRASTIC), and (2) nonnumerical systems in which map units may be numbered in order of increasing vulnerability, or classified as highly vulnerable and less vulnerable. [Table 11.3](#) describes a number of vulnerability mapping techniques and summarizes the type of criteria used. Knox et al. (1993/T11.10) include tables summarizing criteria for the SAFE, WSSIM, HRS, SRM, and PI methods. Perhaps the simplest application of vulnerability mapping for wellhead protection is to develop criteria based on local conditions for defining highly vulnerable hydrogeologic settings (Figure 11.4 and Figure 7.15). The DRASTIC criteria in Worksheet D-W6, the information in [Table 11.3](#), and the references indexed in [Table 11.10](#) may be useful for developing locally appropriate vulnerability criteria.

11.2.4 Selection of Delineation Methods

The state wellhead protection coordinator should be contacted to determine if there is any state guidance regarding the methods that can or should be used to delineate WHPAs. For example, [Table 11.4](#) presents proposed guidance from the state of Georgia identifying generic wellhead

Table 11.3 Summary of Major Ground Water Vulnerability Mapping Methods

Description	Major Vulnerability Criteria	References ^a
<p>DRASTIC method can be applied in any hydrogeologic setting; results in a numerical index based on the sum of weighted ratings for seven criteria; most widely used method</p> <p>Illinois ground-water aquifer vulnerability maps and geographic information system; subsurface geologic data to a depth of 50 ft have been digitized to develop a statewide stack-unit map</p>	<p>See Worksheet D-W6; highly vulnerable, II150 (U.S. EPA, 1986a)</p> <p>Has been used for a variety of applications; Uhlman and Smith (1990) defined eight classes for LUST contamination potential based on depth to uppermost aquifer and presence or absence of major aquifer at depth; highly vulnerable: aquifer material within 5 ft of land surface, variable underlying materials and major aquifer at depth</p>	<p>Aller et al. (1987); <u>Case studies: See Table 11.10</u></p> <p>See Table 11.10</p>
<p>Karst limestone areas are highly vulnerable by definition because conduit flow allows rapid travel of contaminants; several schemes provide more detailed criteria for assessing relative vulnerability</p>	<p>Quinlan et al. (1992b): hypersensitive = high point recharge, high conduit flow, low soil storage (Figure 7.15); Schuster et al. (1989): highly vulnerable = shallow or exposed fracture dolomite bedrock, permeable soils, open surface fractures, sinkholes (Figure 11.4)</p>	<p>Quinlan et al. (1992b), Schuster et al. (1989), Sendlein (1992)</p>
<p>Vulnerability to contamination by agricultural chemicals; various vulnerability indexes have been developed.</p>	<p>DRASTIC pesticide index places greater weight on soil media and topography (Worksheet D-W6); RAVE index (DeLuca and Johnson, 1990) uses a numerical index based on depth to ground water, soil texture, percent organic matter, topographic position, distance to surface water, cropping practice, pesticide application frequency/method, and pesticide leaching index; scores > 60 indicate high concern</p>	<p>Others include the pesticide index (PI) — Rao et al. (1985), U.S. EPA (1986d); SAFE (soil/aquifer field evaluation) — Roux (1986); see Table 11.10 for additional case study references</p>
<p>Numerous schemes have been developed to assess site suitability for solid/hazardous waste land disposal siting or risk from currently contaminated sites; such suitability ranking systems can also be used to assess ground-water vulnerability</p>	<p>LSR (landfill site rating) system uses (1) hydraulic conductivity, (2) sorption, (3) aquifer thickness, (4) depth and gradient of water table, (5) topography, and (6) distance to wells or streams; high suitability = low vulnerability to ground water contamination; low suitability = high vulnerability to ground water contamination; each method has slightly different criteria</p>	<p>LSR: LeGrand (1964, 1983), LeGrand and Brown (1977); HRS (hazard ranking system): Caldwell et al. (1981); SRM (Superfund site rating methodology): Kufs et al. (1980), U.S. EPA (1989, 1991c); SIA (surface impoundment assessment method): Silka and Swearingen (1978), U.S. EPA (1983); WSSIM (waste–soil–site interaction matrix): Phillips et al. (1977)</p>
<p>General ground-water classification schemes</p>	<p>Criteria vary depending on the objective of the classification scheme</p>	<p>General: U.S. EPA (1985, 1986a); sole aquifer program: U.S. EPA (1988b)</p>

^a See Table 11.10 references for full citations.

Source: Boulding (1994).

Table 11.4 Generic WHPAs Proposed for Georgia (Georgia Department of Natural Resources, 1992)

Control Zone	
All Wells	
Impervious surface (pavement)	15 ft
Pervious surface (soil)	25 ft
Inner Management Zone	
All Wells	
Confined aquifer wells	100 ft
Unconfined aquifer wells	250 ft
Karst aquifer wells	500 ft
Outer Management Zone	
Piedmont and Blue Ridge (crystalline rocks)	
Pumping rate	Radius of outer management zone determined by Heath method
Karst Valley and Ridge and Coastal Plain (unconfined aquifer)	
Hydrogeologic mapping	
Coastal Plain (unconfined or partially confined porous media)	
Five-year time-of-travel or volumetric calculations	
Coastal Plain (completely confined aquifer)	
None	

protection areas: (1) a fixed-radius “control zone” in the immediate vicinity of all wells; (2) a fixed-radius “inner management zone” based on whether the aquifer is confined, unconfined, or karst; and (3) an “outer management zone” for which different delineation methods are specified, depending on the hydrogeologic setting. Methods used for delineating the outer management zone include (1) graphical determination of radius based on pumping rate in crystalline rock aquifers (Figure 11.5), (2) hydrogeologic mapping in karst aquifers, and (3) 5-year time-of-travel or volumetric calculations in unconfined or partially confined porous media aquifers.

The Idaho wellhead protection program, on the other hand, identifies four major zones within a wellhead protection area, with a fixed radius used to Zone IA (Table 11.5). Zones IB and Zone II are delineated based on time of travel using hydrogeologic mapping and semianalytical, analytical, or numerical modeling based on site-specific data. Finally, Zone III includes known recharge areas and flow boundaries based on hydrogeologic mapping.

Table 11.1 summarizes the relative advantages and disadvantages of the major methods for delineating WHPAs. Figure 11.6 provides a flowchart for delineating a WHPA. Relevant worksheets in Appendix D are identified in this figure, which shows that some form of hydrogeologic mapping is required for any WHPA delineation effort. At a minimum, this would involve collecting and compiling existing data and maps of the area (Worksheet D-W2). Collection of additional data, as needed, is ongoing at each step in the process. State wellhead protection programs may specify or provide guidance in selecting criteria (i.e., time-of-travel isochrones, drawdown limits) for delineating WHPAs using simple analytical methods or computer models.

Use of multiple approaches to delineating a WHPA (i.e., moving as far through the flowchart in Figure 11.6 as time and financial resources allow) increases the likelihood that the area delineated

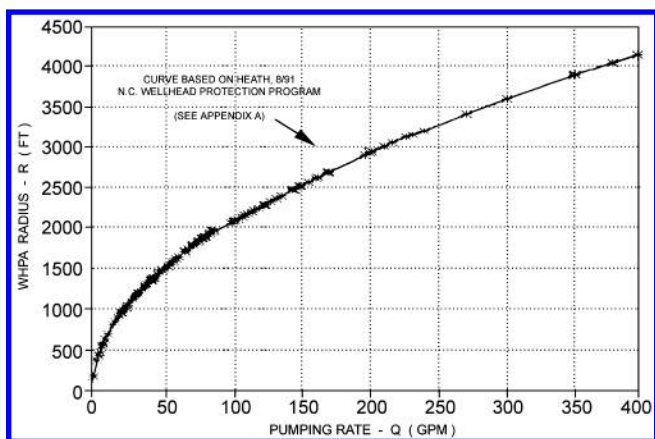


Figure 11.5 Radius of outer management zone based on pumping rate for crystalline aquifers, Piedmont and Blue Ridge (Georgia Department of Natural Resources, 1992).

Table 11.5 Zones for WHPAs in Idaho (Idaho Wellhead Protection Work Group, 1992)

Zone	Criteria and Thresholds	Methods
Zone IA	Minimum distance of 50 ft for wells; minimum distance of 100 ft for springs	Fixed radius
Zone IB	Two-year time of travel	Hydrogeologic mapping and semianalytical, analytical, or numerical modeling using site-specific data
Zone II	Five-year time of travel	Hydrogeologic mapping and semianalytical, analytical, or numerical modeling using site-specific data
Zone III	Known recharge areas and flow boundaries	Hydrogeologic mapping

excludes areas that do not actually contribute ground water to the well. Two situations that might require using more sophisticated delineation methods, such as computer modeling, include (1) the presence of a large number of potential sources of contamination, and (2) the presence of strong opposition to regulatory controls for wellhead protection. In the first situation, the use of more sophisticated methods may avoid unnecessary effort devoted to inventorying potential contaminant sources outside the zone of contribution. In the second case, opposition may be partly defused by excluding areas from regulatory controls that might otherwise have been included. More sophisticated methods are also easier to defend against legal challenge.

11.3 IDENTIFICATION OF POTENTIAL CONTAMINANT SOURCES

The WHPA delineated methods described in the preceding section provide the focus for efforts to identify potential sources of contamination. The inventory should be comprehensive and should include:

- Potential point sources (underground storage tanks, wells, small commercial and industrial facilities, etc.)
- Potential line sources (sewer lines, gas/petroleum pipelines, highways with traffic that may haul hazardous chemicals, etc.)
- Potential area sources (waste disposal areas, agricultural lands receiving fertilizer and pesticide treatments, etc.)

The inventory should identify the type of source, location, and types of potential contaminants at each source. The next section provides detailed checklists for identifying potential sources. Identification of *active* potential sources is relatively straightforward. Location of *inactive* sources,

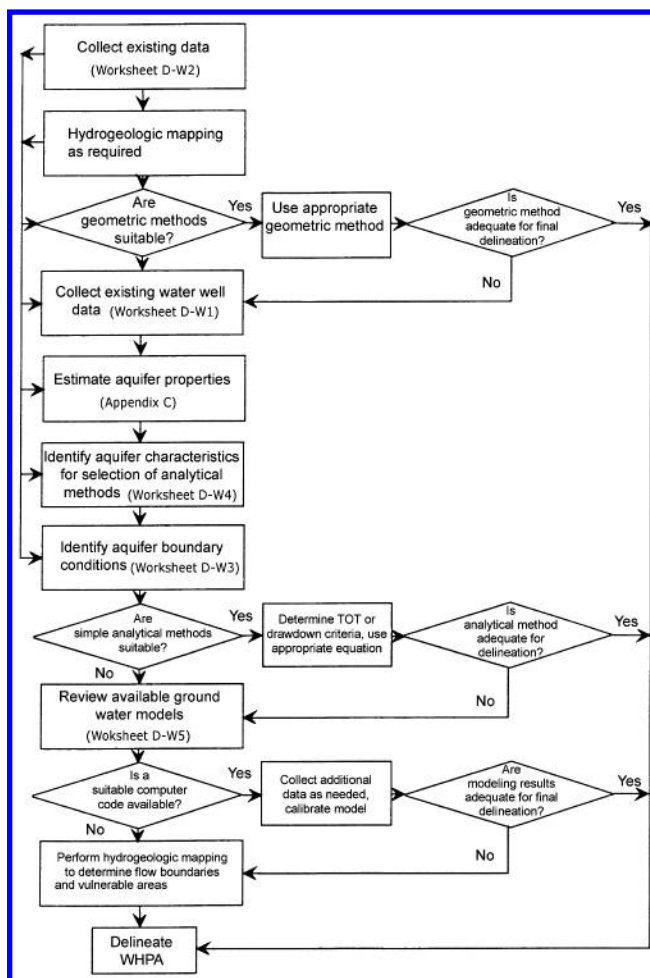


Figure 11.6 Flowchart for selection of wellhead protection delineation methods (Boulding, 1994).

such as abandoned wells and old waste disposal sites, might require some detective work. All existing maps and sources of information on past human activity in the area should be gathered and reviewed. Interviews with long-time residents in the area could yield valuable information that cannot be obtained in any other way. In areas with a long history of oil and gas exploration and production, or where the exact boundaries of old waste disposal sites are not known, surface geophysical methods and other field investigation techniques might be required to locate and map abandoned features. Table A.1 provides summary information on potential surface geophysical methods. Table 4.4 identifies references that provide more detailed information on methods for locating abandoned wells.

A convenient way to compile the results of the inventory is to assign each source an identification number and plot the identification number on a map of the WHPA. The boundaries of the areal sources should be clearly marked on the map. Repetition of the identifying number along a line source provides a means for distinguishing different types of sources. This map provides the focus for subsequent protective strategy development and land management activities.

Where a large number of commercial and industrial sites with potential contaminants are located within a WHPA, a phased approach may be desirable. The first phase would focus on identifying all potential sources, but would not necessarily involve collection of detailed information of all sites. This information would then be screened to identify sites where contaminants represent a

significant potential risk based on the preliminary inventory. In the second phase, these sites would then be revisited to collect more detailed information. The final step in this stage of the wellhead protection process would be to evaluate the degree of threat posed by each source ([Section 11.4](#)).

11.3.1 Step-by-Step Inventory Procedures

Hundreds of nonindustrial, commercial, and industrial activities that produce or use organic and inorganic substances pose a potential threat to ground-water quality. The number of potential contaminants of concern for a given activity may be restricted to a few or many substances. A single comprehensive list of these activities for inventory purposes would be so large as to be unmanageable. This guide offers a four-step approach to developing an inventory of potential sources of contamination within a WHPA:

1. Checklist D-C1 provides a short list of four major categories of potential contamination sources. A “yes” or “uncertain” answer to any of the questions within a major category on this checklist means that the detailed checklist for that category should be used (see next step).
2. Checklists D-C2 through D-C5 provide comprehensive lists of activities that may result in ground-water contamination. The first two (cross-cutting sources and nonindustrial sources) will probably be required for most WHPAs. In rural areas, the use of the remaining checklists may not be required. [Sections 11.3.2](#) through [11.3.3](#) provide additional discussion on these checklists.
3. More detailed information should be compiled for each item that is identified within the WHPA. The following worksheets in Appendix D may provide assistance in gathering information on specific sources: (1) Worksheet D-W7 (Residential Potential Contaminant Source Inventory); (2) Worksheet D-W8 (Farm Potential Contaminant Source Inventory); (3) Worksheet D-W9 (Transportation Hazard Inventory); and (4) Worksheets D-W10 and D-W11 (Municipal/Commercial/Industrial Potential Contaminant Source Inventory: Short and Long Forms). Worksheet D-W1 can be used to compile information on active and abandoned wells.
4. A separate inventory worksheet should be filled out for each household or business by contacting the resident, owner, or other responsible party. Files maintained by the Local Emergency Planning Committee (LEPC) established under Title III of SARA (the Emergency Planning and Community Right-to-Know Act (EPCRA)) should also be consulted. These files identify locations where hazardous chemicals are stored and used. [Table 11.10](#) identifies references that provide more information on collection and analysis of information collected pursuant to EPCRA.

Many state wellhead protection programs have developed their own checklists, worksheets, and inventory forms for identifying potential contaminant sources. The checklists and worksheets in Appendix D represent a synthesis based on review materials developed by state programs as of late 1993. Any of these and state materials, as well as any subsequently developed, can be used as an alternative to or in combination with the materials in Appendix D. This is a complex topic in which improvements are always possible. The best approach is probably to compare the latest materials available for the state’s wellhead protection program with the material in Appendix D and select the materials that seem most appropriate for the WHPA of interest. Alternatively, materials should be modified if comparisons show that no single checklist, worksheet, or inventory form addresses all the information needs for the WHPA.

A Few Words about Natural Contamination Sources. The checklists in this chapter do not address contamination sources that result from natural processes. In some areas, particularly in arid and semiarid areas of the western U.S., ground water is of marginal quality, or exceeds drinking water standards for elements such as arsenic, chloride, fluoride, heavy metals, and radionuclides. Little can be done to prevent such contamination, so the options are essentially limited to finding an alternative, higher quality source of drinking water, or treatment to remove contaminants. Human activity may cause degradation of ground water from natural sources. Examples include mobilization of heavy metals and radionuclides by mining activities and saltwater intrusion into freshwater aquifers by pumping. Such activities are included in the checklists in Appendix D.

11.3.2 Cross-Cutting Sources: Wells, Storage Tanks, and Waste Disposal

Checklist D-C2 identifies three major sources of potential contamination: (1) wells and related features, (2) storage tanks, and (3) waste disposal sites. These are called cross-cutting sources because they may be associated with any of the activities identified in the detailed checklists for nonindustrial, commercial, and industrial sources. The high risk of ground water contamination from storage tanks, especially underground storage tanks, and waste disposal sites is another reason for placing them in a separate checklist.

11.3.3 Nonindustrial Sources

Checklist D-C3 identifies five major categories of potential contamination sources that can be broadly classified as nonindustrial: (1) agricultural, (2) residential, (3) other green areas, (4) municipal and other public services, and (5) transportation. The category of “other green areas” includes any nonagricultural and nonresidential area where grass and other vegetation may receive regular applications of agricultural chemicals. In the residential category, each individual in each residence or living unit should be interviewed, if possible, and a household hazardous waste inventory prepared. Such interviews should increase awareness by individuals and families living within a WHPA of ground-water concerns, and should lay the groundwork for any future public education efforts.

11.3.4 Commercial and Industrial Sources

Checklists D-C4 and D-C5 identify more than 90 commercial and industrial activities that present potential for ground-water contamination. Commercial activities are generally service and sales oriented, while industrial activities involve primarily processing and manufacturing. In practice, the dividing line is not always clear, so both checklists should be examined if the classification of an identified source is uncertain. Commercial activities associated with transportation are included in Checklist D-C3.

Checklist D-C4 identifies three major categories of activities: (1) commercial services and sales; (2) activities related to processing and storage of natural products (food, other animal products, and wood); and (3) resource extraction activities. Checklist D-C5 identifies three major categories of industrial activities: (1) chemical processing and manufacturing; (2) metal manufacturing, fabrication, and finishing; and (3) other manufacturing.

A wide array of potential contaminants are associated with commercial and industrial activities. The U.S. EPA has developed a series of information sheets, available from the RCRA Hotline (Table 5.3), on 17 business activities that may generate hazardous wastes (U.S. EPA, 1990a/T4.4). Checklists D-C4 and D-C5 indicate activities covered by these summary sheets with the EPA document order number. Table 4.4 provides an index to major references that identify types of contaminants associated with major types of activities. The waste minimization and pollution prevention guides described in [Section 11.1.1](#) are also good sources for identifying types of contaminants associated with specific types of manufacturing and commercial activities. [Table 11.6](#) identifies EPA reference sources where more detailed information can be obtained on potential contaminants for industries for which EPA has developed effluent limitation guidelines.

11.4 ASSESSING THE RISK FROM POTENTIAL CONTAMINANTS

Methods for evaluating the risk posed by potential contaminant sources within a WHPA can range from a relatively simple process — classifying sources as high, moderate, and low risk — to a comprehensive risk assessment process in which fate and transport of chemicals of concern

Table 11.6 Index to Development Documents for Effluent Limitation Guidelines for Selected Categories (U.S. EPA, 1987c)

Industrial Point-Source Category	Subcategory	EPA Publication Document No.	NTIS Accession No.	GPO Stock No.
Aluminum forming	Aluminum forming	EPA 440/1-84/073 Vol. I Vol. II	PB84-244425 PB84-244433	— —
Asbestos manufacturing	Building, construction, and paper Textile, friction materials, and sealing devices	EPA 440/1-74/017a EPA 440/1-74/35a	PB238320/6 PB240860/7	5501-00827 —
Battery manufacturing	Battery manufacturing	EPA 440/1-84/067 Vol. I Vol. II	PB85-121507 PB85-121515	— —
Builders' paper and board mills	Pulp, paper and paperboard, and builders' paper and board mills	EPA 440/1-82/025	PB83-163949	—
Canned and preserved fruits and vegetables	Apple, citrus, and potato processing	EPA 440/1-74/027a	PB238649/8	5501-00790
Canned and preserved seafood processing	Catfish, crab, and shrimp Fishmeal, salmon, bottom fish, sardine, herring, clam, oyster, scallop, and abalone	EPA 440/1-74/020a EPA 440/1-75/041a	PB238614/2 PB256840/0	5501-00920 —
Cement manufacturing	Cement manufacturing	EPA 440/1-74/005a	PB238610/0	5501-00866
Coil coating	Coil coating Phase I Coil coating Phase II, can making	EPA 440/1-82/071 EPA 440/1-83/071	PB83-205542 PB84-198647	— —
Copper forming	Copper	EPA 440/1-84/074	PB84-192459	—
Dairy products processing	Dairy products processing	EPA 440/1-74/021a	PB238835/3	5501-00898
Electroplating and metal finishing	Copper, nickel, chrome, and zinc Electroplating — pretreatment Metal finishing	EPA 440/1-74/003a EPA 440/1-79/003 EPA 440/1-83/091	PB238834/AS PB80-196488 PB84-115989	5501-00816 — —
Ferroalloy	Smelting and slag processing	EPA 440/1-74/008a	PB238650/AS	5501-00780
Fertilizer manufacturing	Basic fertilizer chemicals Formulated fertilizer	EPA 440/1-74/011a EPA 440/1-75/042a	PB238652/AS PB240863/AS	5501-00868 5501-01006
Glass manufacturing	Pressed and blown glass Insulation fiberglass Flat glass	EPA 440/1-75/034a EPA 440/1-74/001b EPA 440/1-77/001c	PB256854/1 PB238078/0 PB238-907/0	5501-01036 5501-00781 5501-00814
Grain mills	Grain processing Animal feed, breakfast cereal, and wheat	EPA 440/1-74/028a EPA 440/1-74/039a	PB238316/4 PB240861/5	5501-00844 5501-01007
Inorganic chemicals manufacturing	Inorganic chemicals Phase I Inorganic chemicals Phase II	EPA 440/1-82/007 EPA 440/1-84/007	PB82-265612 PB85-156446/XAB	— —
Iron and steel manufacturing	Iron and steel Vol. I Vol. II Vol. III Vol. IV Vol. V Vol. VI	EPA 440/1-82/024 EPA 440/1-82/024 EPA 440/1-82/024 EPA 440/1-82/024 EPA 440/1-82/024 EPA 440/1-82/024	PB82-240425a PB82-240433b PB82-240441c PB82-240458d PB82-240466e PB82-240474f	—
Leather tanning	Leather tanning	EPA 440/1-82/016	PB83-172593	—

Table 11.6 Index to Development Documents for Effluent Limitation Guidelines for Selected Categories (U.S. EPA, 1987c) (*Continued*)

Industrial Point-Source Category	Subcategory	EPA Publication Document No.	NTIS Accession No.	GPO Stock No.
Meat products and rendering	Red meat processing	EPA 440/1-74/012a	PB238836/AS	5501-00843
	Renderer	EPA 440/1-74/031d	PB253572/2	—
Metal finishing	Metal finishing	EPA 440/1-83/091	PB84-115989	—
Metal molding and casting (foundries)	Metal molding and casting	EPA 440/1-85/070	PB86-161452/XAB	—
Nonferrous metals forming	Nonferrous metals forming	EPA 440/1-84/019b	—	—
		Vol. I	PB83/228296	
		Vol. II	PB83/228304	
		Vol. III	PB83/228312	
Nonferrous metals manufacturing	Bauxite refining — aluminum segment	EPA 440/1-74/019c	PB238463/4	5501-00116
	Primary aluminum smelting — aluminum segment	EPA 440/1-74/019d	PB240859/9	5501-00817
	Secondary aluminum smelting — aluminum segment	EPA 440/1-74/019e	PB238464/2	5501-00819
Organic chemical manufacturing and plastics and synthetic fibers	Organic chemicals manufacturing and plastics and synthetic fibers	EPA 440/1-87-009	Available from NTIS after publication (1/87)	—
Petroleum refining	Petroleum refining	EPA 440/1-82/014	PB83-172569	—
Pharmaceuticals	Pharmaceutical	EPA 440/1-83/084	PB84-180066	—
Phosphate manufacturing	Phosphorous-derived chemicals	EPA 440/1-74/006a	PB241018/1	5503-00078
	Other nonfertilizer chemicals	EPA 440/1-75/043	—	—
Porcelain enameling	Porcelain enameling	EPA 440/1-82/072	—	—
Pulp, paper, and paperboard	Unbleached kraft and semichemical pulp	EPA 440/1-74/025a	PB238833/AS	—
	Pulp, paper and paperboard, and builders' paper and board mills	EPA 440/1-82/025	PB83-163949	—
Rubber processing	Tire and synthetic	EPA 440/1-74/013a	PB238609/2	5501-00885
	Fabricated and reclaimed rubber	EPA 440/1-74/030a	PB241916/6	5501-01016
Soaps and detergents	Soaps and detergents	EPA 440/1-74/018a	PB238613/4	5501-00867
Sugar processing	Beet sugar	EPA 440/1-74/002b	PB238462/6	5501-00117
	Cane sugar refining	EPA 440/1-74/002c	PB238147/3	5501-00826
Textile mills manufacturing	Textile mills	EPA 440/1-82/022	PB83-116871	—
Timber products processing	Wood furniture and fixtures	EPA 440/1-74/033a	—	—
	Timber products processing	EPA 440/1-81/023	PB81-227282	—

Note: This list includes only "final" development documents for effluent limitations guidelines. For many industries, these documents are in the draft or proposal stage.

are modeled to quantify exposure and risk to people or ecosystems. This section focuses on relatively simple ranking methods for evaluating risk and briefly discusses situations in which more complex methods may be required.

11.4.1 Risk Ranking Methods

Classifying potential contaminant sources into risk categories (high, medium, low) is the simplest way to identify the sources within a WHPA that pose a threat to ground-water quality.

Land Use Considerations	Potential Contaminants															
	Acids	Bases	Chloride	Fluoride	Iron/Manganese (sol'n)	Metal (mostly Fe & Mn)	Nitrate	Pathogens (Virus/Bacteria)	Pesticides/Herbicides	Perchlorate	Phenols	Radionuclides	Sodium	Solvents	Sulfide	Sulfonates (Detergents)
Overall Threat to Public Health	L-M	L-M	L	L	L	H	M	L	H	H	H	H	L	H	L	L
Mobility	M	L	H	H	M	LH	H	L	LH	M	M	LH	H	H	H	H
Natural Background																
Land Use Categories																
Agriculture/Golf Courses																M
Airports																M-H
Asphalt Plants																L-M
Beauty Parlors																L
Boat Yards/Builders																L
Car Washes																L
Cemeteries																L
Chemical Manufacture																H
Clandestine Dumping																H
Dry Cleaning																H
Furniture Stripping and Painting																M
Hazardous Materials Storage and Transfer																H
Industrial Lagoons and Pits																H
Jewelry and Metal Plating																M
Junkyards																L
Landfills																H

Figure 11.7 Land use/public supply well pollution potential matrix (Noake, 1988). (Continued on facing page.)

Figure 11.7 illustrates a matrix developed by the Cape Cod Aquifer Management Project to evaluate pollution potential from 32 land use categories. The top of the matrix contains ratings for 16 groups of chemicals according to (1) overall threat to public health, (2) mobility, (3) and whether they may occur naturally in significant concentrations. The overall threat to public water supply for each land use category in Figure 11.7 is rated as low (L) to high (H) in the right-hand column, based on the number of potential contaminants associated with the category and the potential threat posed by each contaminant.

Following the approach in Figure 11.7, once the potential contaminant source inventory has been completed (Section 11.3), each land use category or individual source is placed in a risk category. Figure 11.7 has five categories (low, low–medium, medium, medium–high, and high), but fewer categories (low, medium, and high) can also be used. Figure 11.7 and Checklist D-C6, which identifies high and moderate risk land use activities based on ratings from a variety of sources, can provide some guidance in how to classify potential contaminant sources within a wellhead protection area. Not all sources agree in their classification of specific land use categories, and classification decisions should consider all factors particular to the wellhead protection area in question.


Aquifer vulnerability mapping, as described in Section 11.2.3, is a valuable complement to the risk ranking approach to evaluating potential contaminant sources. For example, any given potential contaminant source represents a less significant threat to a highly confined aquifer than to an unconfined aquifer (see Section 7.5.3).² Table 11.10 identifies a number of references that discuss vulnerability mapping in the context of risk assessment.


Whether a land use is classified as high or moderate risk becomes a significant consideration when developing options for managing the WHPA. High-risk land uses are frequently prohibited in high priority wellhead protection areas, and moderate-risk land uses are commonly restricted in




²An exception to this would be where the source is near an improperly abandoned well that provides a pathway from the surface to the confined aquifer.

Land Use Considerations	Potential Contaminants															
	Acids	Bases	Chloride	Fluoride	Iron/Manganese (Fe/Mn)	Metals (except Fe & Mn)	Nitrate	Pathogens (Vib. Bacteroid)	Pesticides/Herbicides	Petroleum Products	Phenols	Radioactivity	Sodium	Solvents	Sulfate	Surfactants (Detergents)
Overall Threat to Public Health	L-M	L-M	L	L	L	H	M	L	H	H	H	H	L	H	L	L
Mobility	M	L	H	H	M	LH	H	L	LH	M	M	LH	H	H	H	H
Natural Background																
Land Use Categories																Overall Threat to Public Water Supply
Laundromats																L-M
Machine Shops/Metal Working																H
Municipal Wastewater/Sewer Lines																H
Photography Labs/Printers																L-M
Railroad Tracks and Yards Maintenance /Stations																M
Research Labs/Universities/Hospitals																L-M
Road and Maintenance Depots																M
Sand and Gravel Mining/Washing																L
Septage Lagoons and Sludge																H
Septic Systems, Cesspools and Water softeners																H
Stables, Feedlots, Kennels, Piggeries, Manure Pits																M-H
Stormwater Drains/Retention Basins																L-M
Stump Dumps																L
Underground Storage Tanks																H
Vehicular Services																H
Wood Preserving																L

Key to Figure 11-7

 The contaminant(s) released from this land-use category *may render* groundwater at a public-supply well undrinkable in accordance with federal and state maximum contaminant levels.

 This land use category is not generally associated with the release of the particular contaminant in quantities that would render the groundwater at a public-supply well undrinkable. However, the contaminant may be associated with a particular activity

 = Low Threat  = Medium Threat  = High Threat

This Matrix is based on a literature review and the combined field experience of the Cape Cod Aquifer Management Project (CCAMP). **THIS MATRIX SHOULD BE USED AS A GUIDE AND HANDY REFERENCE.** It is not a substitute for looking at a particular land use in detail. There will always be the potential for a business to use an unusual process using chemicals not normally associated with that business. The land-use categories included in the Matrix and *Guide to Contamination Sources for Wellhead Protection* are those that might be found in the primary recharge area of a public-supply well in Massachusetts. This Matrix may be misleading or erroneous if applied to low-yield private wells.

- Nitrate has a cumulative impact on groundwater quality. No one category is responsible for the release of nitrate. A variety of land use categories release nitrate. These include animal feedlots, landfills, septic systems, septage lagoons, municipal wastewater and agricultural activities including turf maintenance.
- There are no known instances of beauty parlors contaminating well water in Massachusetts. More research is needed to determine the severity of a threat to groundwater from this land use category.
- Refer to *Guide to Contamination Sources for Wellhead Protection*, pp. 1-2.

Figure 11.7 Continued.

such areas. Table 11.7 illustrates how particular high- and moderate-risk land uses have been either prohibited or restricted (i.e., special permit required) in four water resource protection zones on Nantucket Island. High-risk activities are either prohibited (P) or a special permit is required (SP). In the most sensitive areas (WR1), all high-risk activities are prohibited, whereas in the least sensitive areas (WR4), all high-risk activities require a special use permit. High-risk activities in water resource protection zones of intermediate sensitivity are prohibited or require a special permit, depending on the activity.

Table 11.7 Regulated Land Uses in Different Water Resource Protection Zones, Nantucket Island, MA (Horsley, 1990)^a

Land Use	WR1	WR2	WR3	WR4
1. Sanitary landfills	P	P	P	SP
2. Junk yards, salvage yards	P	P	P	SP
3. Municipal sewage treatment facilities with on-site disposal of primary or secondary treated effluent	P	P	P	SP
4. Car and truck washes	P	P	SP	SP
5. Road salt stockpiles	P	P	SP	SP
6. Dry cleaning establishments, coin or commercial laundries	P	P	SP	SP
7. Motor vehicle and boat service and repair facilities, including body shops	P	P	P	SP
8. Metal plating establishments	P	P	SP	SP
9. Sales, storage, or disposal of fuels or hazardous chemicals	P	P	P	SP
10. Chemical and bacteriological laboratories	P	P	P	SP
11. Trucking or bus terminals	P	P	P	SP
12. Any use that involves as a principal activity the manufacture, storage, use, transportation, or disposal of toxic or hazardous materials	P	P	SP	SP
13. Any use that involves the use of toxic and hazardous materials in quantities greater than those associated with normal household use	P	P	SP	SP
14. Residential development at densities exceeding those stated in Section E of this bylaw	P	P	P	SP
15. Golf courses	P	SP	SP	SP

Note: P = prohibited; SP = special permit required.

^a See Appendix F for full credit.

11.4.2 Other Risk Evaluation Methods

Risk ranking and aquifer vulnerability mapping methods are probably adequate for many WHPAs. Where many high-risk potential contaminant sources exist within a WHPA, more sophisticated risk assessment approaches may be required to help identify the most efficacious and cost-effective options for reducing risk. Factors that need to be considered for a comprehensive risk assessment include (1) chemical toxicity; (2) pathways that can lead to exposure; (3) the characteristics of the population being exposed (density, age, etc.); (4) the probability that health-threatening exposures will actually occur; (5) the cost of options for reducing risk from exposure; and (6) the perception of risk by the exposed population. [Figure 11.8](#) provides an example diagram of an exposure pathway assessment for a landfill.

The EPA has developed a relatively sophisticated manual procedure to assess and screen relative threats to ground-water supplies posed by potential contaminant sources (U.S. EPA, 1991a/T11.10). The method involves a series of step-by-step procedures using worksheets that result in an overall risk rating for each contaminant source based on (1) the likelihood of well contamination, and (2) the severity of well contamination.

A variety of methods have been developed for evaluating risks addressed by other EPA programs. For example, several methods have been developed to help communities evaluate the risk posed by chemicals that must be reported under EPA's Toxic Release Inventory (TRI) program (FEMA/DOT/EPA, 1989/T11.10; U.S. EPA, 1989b/T11.10). These methods focus more on the risks posed by airborne accidental releases of chemicals. Elements of these methods, however, could be adapted for use in evaluating the risks of ground-water contamination by chemicals reported under the TRI program. Similarly, methods used to assess risk at Superfund sites and for other EPA programs may be useful, under certain circumstances, for evaluating risk in WHPAs. [Table 11.10](#) provides an index to major references on risk assessment in relation to ground-water contamination and other methods for exposure and risk assessment.

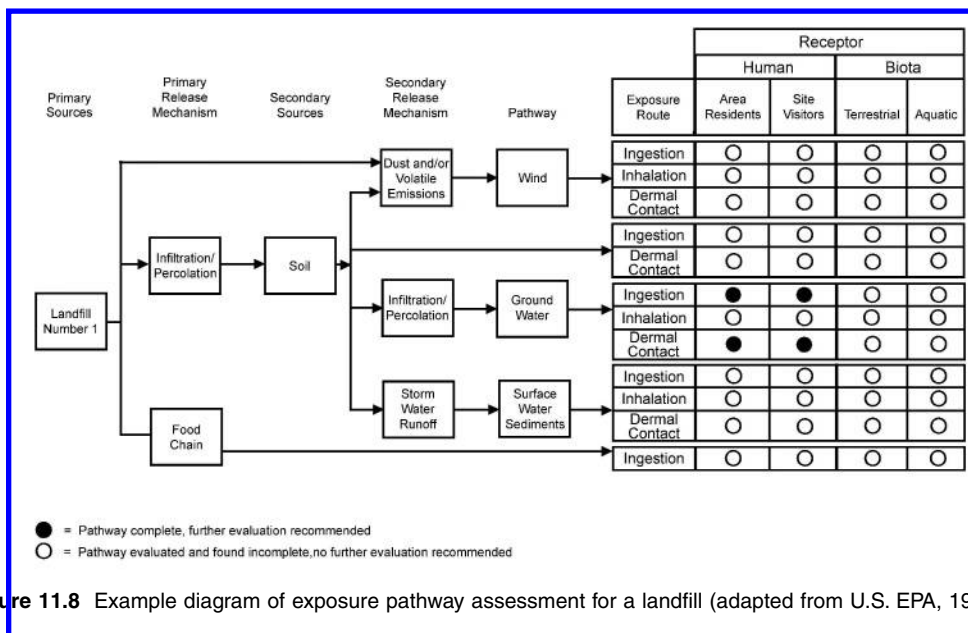


Figure 11.8 Example diagram of exposure pathway assessment for a landfill (adapted from U.S. EPA, 1989a).

11.5 WELLHEAD PROTECTION AREA MANAGEMENT

Management of WHPAs to prevent ground-water contamination involves several steps:

- Identification of protection options appropriate for the types of potential contaminants present
- Selection of those that are technically and politically feasible for the area
- Implementation of the options
- Monitoring of the effectiveness of management and application of additional management practices, if required
- Development of contingency plans to address threats to a water supply as a result of accident or failure of the management practices that have been implemented

11.5.1 General Regulatory and Nonregulatory Approaches

Wellhead protection management options or tools can be broadly classified as *regulatory* and *nonregulatory*. At the local level, regulatory approaches generally involve the use of some form of (1) zoning ordinances, (2) subdivision or individual lot controls, or (3) promulgation of local health and environmental regulations designed to directly or indirectly protect ground water in a WHPA. State-level legislation or regulations may also address wellhead protection. Nonregulatory controls, as the name implies, involve voluntary actions on the part of the public and private sector to enhance ground-water protection.

Wellhead protection management options can also be classified as *technical* and *nontechnical*. Although the dividing line may not always be clear, technical options generally involve controls based on some understanding of the relationship between contaminant characteristics and the hydrogeology of a WHPA. Nontechnical options are generally not directly related to scientific considerations, although indirect relationships exist to the extent that WHPA delineation and contaminant risk assessment processes are scientifically based.

Checklist D-C7 identifies 45 specific wellhead protection tools in three major categories: (1) nontechnical regulatory options, (2) nontechnical nonregulatory options, and (3) technical regulatory and nonregulatory options. Nontechnical options are not discussed further here. However,

Checklist D-C7 indicates where [Table 11.8](#) and [Table 11.9](#) provide summary information on specific options. The rest of this section focuses on general technical approaches to WHPA management (Section 11.5.2) and specific approaches for different types of land use (Section 11.5.3).

11.5.2 General Technical Approaches

Design Standards and Best Management Practices. *Design standards* define specifications for how a building or on-site wastewater disposal system should be constructed. *Best management practices* (BMPs) define how repeated activities, such as construction and farming, should be carried out so as to minimize adverse environmental impacts. The great advantage of these approaches is their simplicity. They establish an objective standard for monitoring compliance. Design standards usually require evaluation of compliance at the time of inspection, although some ongoing monitoring may also be required. BMPs may require ongoing monitoring for compliance. However, design standards and BMPs will provide only adequate protection if the assumptions used in establishing the standard or practice apply within a WHPA. Design standards and BMPs tend to be less flexible than performance standards (next section) because they cannot be readily modified to reflect local conditions.

Performance and Operating Standards. Performance and operating standards focus on establishing measurable environmental standards that protect human health or the environment. Performance and operating standards alone do not specify how performance should be achieved. Determining compliance for environmental standards, such as minimum acceptable concentrations of a chemical in ground water, is relatively simple, requiring sampling and chemical analysis. However, noncompliance will require additional actions to find the reason for noncompliance and the implementation of methods to bring the system back into compliance. This approach generally provides more flexibility than design standards and BMPs, since almost any method can be used, as long as the performance standard is achieved. To be effective, performance and operation standards must be implemented far enough from the wellhead area that noncompliance can be rectified without posing a threat to the well.

Ground-Water Monitoring. Ground-water monitoring is an essential component of wellhead protection. All WHPA delineation methods involve irreducible uncertainties due to the inherent physical and chemical complexity of hydrogeologic systems. Previous chapters have made suggestions for ways to address uncertainties, but no delineation method or ground-water management practice is fail-safe. For early detection of contamination, monitoring wells should be installed between significant point sources of potential contamination and the wellhead area in the most direct ground-water flow path line (Chapter 2). One or more monitoring wells should be installed upgradient of the wellhead along a specified time-of-travel contour (say 2- to 5-year isochrone) to provide an early warning of the presence of contaminants traveling toward the well.

Installation of ground-water monitoring wells and ground-water sampling require special procedures to ensure that samples are representative. Table 9.10 identifies major EPA and other documents that provide guidance in this area.

11.5.3 Specific Regulatory and Technical Approaches

In addition to Checklist D-C7 and [Table 11.8](#) and [Table 11.9](#) discussed earlier, [Figure 11.9](#) provides ratings for the applicability of 10 local regulatory techniques to 34 land use categories.

11.5.4 Contingency Planning

Developing a contingency plan to deal with emergency threats to ground-water quality in the WHPA, such as accidental chemical spills, is an essential part of managing a wellhead protection area. The plan should include information that allows a rapid response to minimize damage from

Table 11.8 Summary of Wellhead Protection Tools (U.S. EPA, 1993)

	Applicability to Wellhead Protection	Land Use Practice	Legal Considerations	Administrative Considerations
		Regulatory: Zoning		
Overlay GW protection districts	Used to map WHPAs; provide for identification of sensitive areas for protection; used in conjunction with other tools that follow	Community identifies WHPAs on practical base/zoning map	Well-accepted method of identifying sensitive areas; may face legal challenges if WHPA boundaries are based solely on arbitrary delineation	Requires staff to develop overlay map; inherent nature of zoning provides "grandfather" protection to preexisting uses and structures
Prohibition of various land uses	Used within mapped WHPAs to prohibit ground-water contaminants and uses that generate contaminants	Community adopts prohibited uses list within their zoning ordinance	Well-organized function of zoning; appropriate techniques to protect natural resources from contamination	Requires amendment to zoning ordinance; requires enforcement by both visual inspection and on-site investigations
Special permitting	Used to restrict uses within WHPAs that may cause ground-water contamination if left unregulated	Community adopts special permit "thresholds" for various uses and structures within WHPAs; community grants special permits for "threshold" uses only if ground-water quality will not be compromised	Well-organized method of segregating land uses within critical resource areas such as WHPAs. Requires case-by-case analysis to ensure equal treatment of applicants	Requires detailed understanding of WHPA sensitivity by local permit granting authority; requires enforcement of special permit requirements and on-site investigations
Large-lot zoning	Used to reduce impacts of residential development by limiting numbers of units with WHPAs	Community "down zones" to increase minimum acreage needed for residential development	Well-recognized prerogative of local government; requires rational connection between minimum lot size selected and resource protection goals; arbitrary large-lot zones have been struck down without logical connection to master plan or WHPA program	Requires amendment to zoning ordinance
Transfer of development rights	Used to transfer development from WHPAs to locations outside WHPAs	Community offers transfer option within zoning ordinance; community identifies areas where development is to be transferred "from" and "to"	Accepted land use planning tool	Cumbersome administrative requirements; not well suited for small communities without significant administrative resources

Table 11.8 Summary of Wellhead Protection Tools (U.S. EPA, 1993) (Continued)

	Applicability to Wellhead Protection	Land Use Practice	Legal Considerations	Administrative Considerations
Cluster/PUD design	Used to guide residential development outside of WHPAs; allows for point-source discharges that are more easily monitored	Community offers cluster/PUD as development option within zoning ordinance; community identifies areas where cluster/PUD is allowed (i.e., within WHPAs)	Well-accepted option for residential land development	Slightly more complicated to administer than traditional grid subdivision; enforcement/inspection requirements are similar to grid subdivision
Growth controls/timing	Used to time the occurrence of development within WHPAs; allows communities the opportunity to plan for wellhead delineation and protection	Community imposes growth controls in the form of building caps, subdivision phasing, or other limitations tied to planning concerns	Well-accepted option for communities facing development pressures within sensitive resource areas; growth controls may be challenged without a rational connection to the resource being protected	Generally complicated administrative process; requires administrative staff to issue permits and enforcement growth control ordinances
Performance standards	Used to regulate development within WHPAs by enforcing predetermined standards for water quality; allows for aggressive protection of WHPAs by limiting development within WHPAs to an accepted level	Community identifies WHPAs and established thresholds for water quality	Adoption of specific WHPA performance standards requires sound technical support; performance standards must be enforced on a case-by-case basis	Complex administrative requirements to evaluate impacts of land development within WHPAs
Regulatory: Subdivision Control				
Drainage requirements	Used to ensure that subdivision road drainage is directed outside of WHPAs; used to employ advanced engineering designs of subdivision roads within WHPAs	Community adopts stringent subdivision rules and regulations to regulate road drainage/runoff in subdivision within WHPAs	Well-accepted purpose of subdivision control	Requires moderate level of inspection and enforcement by administrative staff

Regulatory: Health Regulations

Underground fuel storage systems	Used to prohibit underground fuel storage systems (USTs) within WHPAs; used to regulate USTs within WHPAs	Community adopts health/zoning ordinance prohibiting USTs within WHPAs; community adopts special permit or performance standards for use of USTs within WHPAs	Well-accepted regulatory option for local government	Prohibition of USTs requires little administrative support; regulating USTs requires moderate amounts of administrative support for inspection follow-up and enforcement
Privately owned wastewater treatment plants (small sewage treatment plants)	Used to prohibit small sewage treatment plants (SSTPs) within WHPAs	Community adopts health/zoning ordinance within WHPAs; community adopts special permit or performance standards for use of SSTPs within WHPAs	Well-accepted regulatory option for local government	Prohibition of SSTPs requires little administrative support; regulating SSTPs requires moderate amount of administrative support of inspection follow-up and enforcement
Septic cleaner ban	Used to prohibit the application of certain solvent septic cleaners, a known ground water contaminant, within WHPAs	Community adopts health/zoning ordinance prohibiting the use of septic cleaners containing 1,1,1-trichloroethane or other solvent compounds within WHPAs	Well-accepted method of protecting ground-water quality	Difficult to enforce even with sufficient administrative effort
Septic system upgrades	Used to require periodic inspection and upgrading of septic systems	Community adopts health/zoning ordinance requiring inspection and, if necessary, upgrading of septic systems on a timely basis (e.g., every 2 years) or upon title/property transfer	Well-accepted as within purview of government to ensure protection of ground water	Significant administrative resources required for this option
Toxic and hazardous materials handling regulations	Used to ensure proper handling and disposal of toxic materials/waste	Community adopts health/zoning ordinance requiring registration and inspection of all businesses within WHPA using toxic/hazardous materials above certain quantities	Well accepted as within purview of government to ensure protection of ground water	Requires administrative support and on-site inspections
Private well protection	Used to protect private on-site water supply wells	Community adopts health/zoning ordinance to require permits for new private wells and to ensure appropriate well-to-septic-system setbacks; also requires pump and water quality testing	Well accepted as within purview of government to ensure protection of ground water	Requires administrative support and review of applications

Table 11.8 Summary of Wellhead Protection Tools (U.S. EPA, 1993) (Continued)

	Applicability to Wellhead Protection	Land Use Practice	Legal Considerations	Administrative Considerations
Nonregulatory: Land Transfer and Voluntary Restrictions				
Sale/donation	Land acquired by a community with WHPAs, either by purchase or donation; provides broad protection to the ground water supply	As nonregulatory technique, communities generally work in partnership with nonprofit land conservation organizations	Many legal consequences of accepting land for donation or sale from the private sector, mostly involving liability	Few administrative requirements involved in accepting donations or sales of land from the private sector; administrative requirements for maintenance of land accepted or purchased may be substantial, particularly if the community does not have a program for open-space management
Conservation easements	Can be used to limit development within WHPAs	Similar to sales/donations, conservation easements are generally obtained with the assistance of nonprofit land conservation organization	Same as above	Same as above
Limited development	As the title implies, this technique limits development to portions of a land parcel outside of WHPAs	Land developers work with community as part of a cluster/PUD to develop limited portions of a site and restrict other portions, particularly those within WHPAs	Similar to those noted in cluster/PUD under zoning	Similar to those noted in cluster/PUD under zoning
Nonregulatory: Other				
Monitoring	Used to monitor ground water quality within WHPAs	Communities establish ground-water monitoring program within WHPA; communities require developers within WHPAs to monitor ground-water quality downgradient from their development	Accepted method of ensuring ground water quality	Requires moderate administrative staffing to ensure routine sampling and response if sampling indicates contamination
Contingency plans	Used to ensure appropriate response in cases of contaminant release or other emergencies within WHPAs	Community prepares a contingency plan involving wide range of municipal/county officials	None	Requires significant up-front planning to anticipate and be prepared for emergencies

Hazardous waste collection	Used to reduce accumulation of hazardous materials within WHPAs and the community at large	Communities, in cooperation with the state or regional planning commission, or other entity, sponsor a hazardous waste collection day several times per year	There are several legal issues raised by the collection, transport, and disposal of hazardous waste	Hazardous waste collection programs are generally sponsored by government agencies, but administered by a private contractor
Public education	Used to inform community residents of the connection between land use within WHPAs and drinking water quality	Communities can employ a variety of public education techniques ranging from brochures detailing their WHPA program, to seminars, to involvement in events such as hazardous waste collection days	No outstanding legal considerations	Requires some degree of administrative support for programs, from brochure mailing to more intensive support for seminars and hazardous waste collection days
Legislative				
Regional WHPA districts	Used to protect regional aquifer systems by establishing new legislative districts that often transcend existing corporate boundaries	Requires state legislative action to create a new legislative authority	Well-accepted method of protecting regional ground-water resources	Administrative requirements will vary depending on the goal of the regional district; mapping of the regional WHPAs requires moderate administrative support, while creating land use controls within the WHPA will require significant administrative personnel and support
Land banking	Used to acquire and protect land within WHPAs	Usually accomplished with a transfer tax established by state government empowering local government to impose a tax on the transfer of land from one party to another	Can be subject to legal challenge as an unjust tax, but have been accepted as a legitimate method of raising revenue for resource protection	Require significant administrative support if they are to function efficiently

Table 11.9 Potential Management Tools for Wellhead Protection (Born et al., 1987; U.S. EPA, 1989b)


Regulatory	Nonregulatory
<p>Zoning Ordinances. Zoning ordinances typically are comprehensive land use requirements designed to direct the development of an area. Many local governments have used zoning to restrict or regulate certain land uses within wellhead protection areas.</p> <p>Subdivision Ordinances. Subdivision ordinances are applied to land that is divided into two or more subunits for sale or development. Local governments use this tool to protect wellhead areas in which ongoing development is causing contamination.</p> <p>Site Plan Review. Site plan reviews are regulations requiring developers to submit for approval plans for development occurring within a given area. This tool ensures compliance with regulations or other requirements made within a wellhead protection area.</p> <p>Design Standards. Design standards typically are regulations that apply to the design and construction of buildings or structures. This tool can be used to ensure that new buildings or structures placed within a wellhead protection area are designed so as not to pose a threat to the water supply.</p> <p>Operating Standards. Operating standards are regulations that apply to ongoing land use activities to promote safety or environmental protection. Such standards can minimize the threat to the wellhead area from ongoing activities such as the application of agricultural chemicals or the storage and use of hazardous substances.</p> <p>Source Prohibitions. Source prohibitions are regulations that prohibit the presence or use of chemicals or hazardous activities within a given area. Local governments can use restrictions on the storage or handling of large quantities of hazardous materials within a wellhead protection area.</p> <p>Inspection and Testing. Local governments can use their statutory home rule power to require more stringent control of contaminant sources within wellhead protection areas than given in federal or state rules.</p>	<p>Purchase of Property or Development Rights. The purchase of property or development rights is a tool used by some localities to ensure complete control of land uses in or surrounding a wellhead area. This tool may be preferable if regulatory restrictions on land use are not politically feasible and the land purchase is affordable.</p> <p>Public Education. Public education often consists of brochures, pamphlets, or seminars designed to present wellhead area problems and protection efforts to the public in an understandable fashion. This tool promotes the use of voluntary protection efforts and builds public support for a community protection program.</p> <p>Waste Reduction. Residential hazardous waste management programs can be designed to reduce the quantity of household hazardous waste being disposed of improperly. This program has been used in localities where municipal landfills potentially threaten ground water due to improper household waste disposal in the wellhead area.</p> <p>Best Management Practices. BMPs are voluntary actions that have a long tradition of being used, especially in agriculture. Technical assistance for farmers wishing to apply them is available from local extension and SCS offices.</p> <p>Training and Demonstration. These programs can complement many regulations; for example, training underground storage tank inspectors and local emergency response teams or demonstration of agricultural BMPs.</p> <p>Ground-Water Monitoring. Ground-water monitoring generally consists of sinking a series of test wells and developing an ongoing water quality testing program. This tool provides for monitoring the quality of the ground-water supply or the movement of a contaminant plume.</p> <p>Contingency Plans. Local governments can develop their own contingency plans for emergency response to spills and for alternative water supply in case of contamination of the existing water supply.</p>


accidental spills or other releases of chemicals, such as during efforts to control a fire at a known chemical storage site. The plan should also include short- and long-term solutions to the temporary or permanent loss of all or a portion of the water system source. A contingency plan should include the following elements:


1. Basic information about the water supply system such as population; number of service connections; location of fire hydrants; average daily usage; and the names and telephone numbers of the water system operator, the fire chief, police chief, and other emergency planning officials.
2. A list of potential contaminant sources and their locations ([Section 11.3](#)).
3. A map identifying the WHPA boundaries; how they were delineated; and significant aspects of local hydrogeology, geography, and geology that affect movement of contaminants in the subsurface.
4. Fire-fighting plans for specific sites, especially sites within the WHPA that store or handle toxic chemicals. Such plans should be developed in coordination with the Local Emergency Planning Committee ([Section 11.3.1](#)).

Local Regulatory Techniques (see discussion in Guidebook)											
	Best Management Practices	Overlay Protection District/ Other Zoning Restrictions	Special Use Permits (Under-zoning)	Site Plan Review	Subdivision Control Regulations	Septic System Regulations	Hazardous Materials Regulations	Facility Materials Storage by Law	Facility Operating Plan Review	Public Education and Awareness	
Land Use Categories											
Agriculture											
Airports											
Asphalt Plants											
Beauty Parlors											
Boat Yards/Builders											
Car Washes											
Cemeteries											
Chemical Manufacture											
Clandestine Dumping											
Dry Cleaning											
Furniture Stripping & Painting											
Golf Courses/Turf Management											
Hazardous Materials Storage											
High Technology Industries											
Industrial Lagoons and Pits											
Jewelry and Metal Plating											
Junkyards											
Landfills											
Laundromats											
Machine Shops/Metal Working											
Municipal Wastewater/Sewer Lines											
Photography Labs/Printers											
Railroad Tracks and Yards											
Research Labs/Hospitals											
Road and Maintenance Depots											
Sand and Gravel Mining/Washing											
Septage Lagoons and Sludge											
Septic Systems, Cesspools											
Stables, Feedlots, Kennels											
Stormwater Drains/Retention Basins											
Stump Dumps											
Underground Storage Tanks											
Vehicular Services											
Wood Preserving											

Explanation of the Matrix

 Not Applicable

 Applicable to Proposed Uses

 Applicable to Existing and Proposed Land Uses

This Matrix relates local regulatory techniques to various land use categories. The local authority has options for controlling potential contaminant sources. Each technique can incorporate provisions for existing uses, proposed uses, and other situations, such as a changed use or an abandoned use. Because techniques to control existing uses automatically cover future uses, a box showing applicability to existing uses only does not appear.

Figure 11.9 Wellhead protection land use/local regulatory techniques matrix (Noake, 1988).

5. Surface spill emergency response procedures, including the names and phone numbers of agencies and other individuals outside the community who should be informed. These procedures should be developed in coordination with the Local Emergency Planning Committee ([Section 11.3.1](#)). Information on the type, location, and amount of spill should be recorded.
6. Short-term emergency water supply options, including a brief description of the type and location of water supply and the names and telephone numbers of people who should be contacted in the event that the source must be used.
7. Long-term alternative water supply options.

U.S. EPA (1990c/T11.11) provides general guidance on contingency planning. Many state wellhead protection programs have developed additional guidance. State wellhead protection programs may also have developed guidance documents for development of contingency plans.

11.6 GUIDE TO MAJOR REFERENCES

[Table 11.10](#) provides an index of major references on ground-water vulnerability mapping and chemical hazard and risk assessment (including ecological assessment and environmental/ecotoxicology), and [Table 11.11](#) provides an index to major references on pollution prevention and soil and ground-water protection management. [Section 11.1.1](#) discusses references for site-specific waste minimization. References on ground-water protection management are grouped into the following main categories: (1) general land use planning, (2) ground-water protection, (3) local planning approaches, (4) community decision maker and citizen guides, (5) federal and state programs, and (6) specific approaches.

Table 11.10 Index to Major References on Ground Water Vulnerability Mapping and Chemical Hazard and Risk Assessment

Topic	References
Ground-Water Vulnerability Mapping	
Methods/Criteria	<u>General Reviews</u> : Anderson and Gosk (1987), Bachmat and Collin (1987), Barrocu and Biallo (1993), GAO (1992), Hoffer (1986), Kanivetsky et al. (1991), Knox et al. (1993), NRC (1993, 1994); <u>DRASTIC</u> : Aller et al. (1987); <u>Illinois Stack-Unit System</u> : Berg and Kempton (1984), Berg et al. (1984), Shafer (1985), Soller and Berg (1992); <u>Indiana Hydrogeologic Terrain System</u> : Fleming (1992), Fleming et al. (1993); <u>Waste Disposal Siting</u> : Caldwell et al. (1981 — HRS), Gibb et al. (1983), Halfon (1989), Kufs et al. (1980 — SRM), LeGrand (1964, 1983 — LSR), LeGrand and Brown (1977 — LSR), Phillips et al. (1977 — WSSIM), Silka and Swearingen (1978 — SIA), U.S. EPA (1983 — SIA, 1986b, 1989a — HRS); <u>Other Agricultural Chemical Systems</u> : Curry (1990), DeLuca and Johnson (1990 — RAVE), Holman (1986a, 1986b), Rao et al. (1985 — PI), Roux et al. (1986 — SAFE), Sokol et al. (1993), U.S. EPA (1986c — PI); <u>Karst</u> : Quinlan et al. (1992a, 1992b), Schuster et al. (1989); <u>General Ground Water Classification Schemes</u> : Pettyjohn et al. (1991), U.S. EPA (1985a, 1986a); <u>Sole Source Aquifers</u> : U.S. EPA (1988a)
Applications	<u>Waste Disposal Siting</u> : Gibb et al. (1983); <u>Agricultural Chemicals</u> : Alexander and Liddle (1986), Blanton and Villeneuve (1989), Ehteshami et al. (1991), Holman (1986a, 1986b), Sokol et al. (1993); <u>Karst</u> : Quinlan et al. (1992b), Schuster et al. (1989), Sendlein (1992); <u>Leaking Underground Storage Tanks</u> : Uhlman and Smith (1990)
Case Studies	<u>DRASTIC</u> : Alexander and Liddle (1986), Blanton and Villeneuve (1989), Duda and Johnson (1987), Ehteshami et al. (1991), FDER (undated), LeGrand and Rosen (1992), Pima Association of Governments (1992), Rosen (1994), Sendlein (1992), Soller (1992); <u>Illinois Stack-Unit System</u> : Kempton and Cartwright (1984), Uhlman and Smith (1990)
Chemical Hazard and Risk Assessment	
Chemical Hazards	Conway (1982), FEMA/DOT/EPA (1989), U.S. Department of Agriculture Extension Service (1989), U.S. EPA (1988b, 1988f, 1989b, 1990f, 1992b); <u>Estimating Chemical Releases</u> : See industrial/commercial contaminant source references in Table 4.4, U.S. EPA (1992a); <u>Chemical Hazard Identification</u> : NIOSH (1990), U.S. DOT (1993)
Risk Communication	Sadar and Shull (199), Sandman (1986), U.S. EPA (1987–1989, 1988j, 1988k, 1989c, 1989p, 1990a)
SARA Title III ^a	<u>General</u> : U.S. EPA (1988b, 1988e, 1989f, 1989g, 1989h, 1989i, 1990b, 1992b); <u>Emergency Planning</u> : U.S. EPA (1987b, 1988g, 1988h, 1988i, 1990d)
Exposure Assessment	
General	California Department of Health Services (1990), Neely (1994), U.S. EPA (1986–1988, 1988c, 1990i), Wang (1994)
Other	<u>Biomarkers</u> : Saleh et al. (1994); <u>Dermal Exposure</u> : U.S. EPA (1992i); <u>Exposure Factors</u> : AIHC (1994), Schaum (1990), U.S. EPA (1985b, 1989j, 1991a, 1991d, 1991e); <u>Food Contamination Pathways</u> : U.S. EPA (1986f); <u>Models/Methods</u> : Bird et al. (1991 — TEEAM)
Risk Assessment	
General	Asante-Duah (1993), Benjamin and Belluck (2001), California Department of Health Services (1990), California Department of Toxic Substances Control (1992, 1994), Cothorn (1996), CRAM (1993), Frantzen (2001), Gorsuch et al. (1993), Gots (1992), Mertz et al. (1994), National Research Council (1983), Neely (1994), Rail (2000), Renzoni et al. (1994), U.S. EPA (1986–1988, 1987a, 1993a — bibliography), Wang (1994); <u>Information Sources</u> : U.S. EPA (1986e); <u>Biological Values</u> : U.S. EPA (1988d); <u>Data Useability</u> : U.S. EPA (1990g, 1992c); <u>Case Studies</u> : Paustenbach (1989); <u>Superfund Risk Assessment</u> : Hoddinott (1993, 1996), U.S. EPA (1986d, 1991b, 1992c)
Ground Water	<u>Texts/Reports</u> : McTernan and Kaplan (1990), Reichard et al. (1990), Trojan and Perry (1989), U.S. EPA (1991); <u>Papers</u> : Flanagan et al. (1991), Pfannkuch (1991)

Table 11.10 Index to Major References on Ground Water Vulnerability Mapping and Chemical Hazard and Risk Assessment (*Continued*)

Topic	References
Ecological Assessment	Bartell et al. (1992), Cairns et al. (1992), Calabrese and Baldwin (1993), Eastern Research Group (1991), Icf. (1988), Maughn (1993), Norton et al. (1988), Renzoni et al. (1994), Suter (1993), Suter et al. (2000), USDI (1987b, 1987c), U.S. EPA (1989e, 1989k, 1989l, 1989m, 1989n, 1990h, 1991f, 1992d, 1992e, 1992g, 1993b); <u>Bioassessment Field/Laboratory Methods</u> : EPRI (1985), U.S. EPA (1989o, 1990k, 1992h, 1993c), USFWS (1989), Warren-Hicks et al. (1989); <u>Ecological Indicators/Functional Values</u> : U.S. EPA (1990j, 1992f), USFWS (1984)
Chemical Toxicity Properties	ATSDR (2001), Cherimisinoff (1999), Cherimisinoff et al. (1994), Derelank and Hollinger (2002), Kamrin (1997 — pesticides)
Environmental Toxicology	Cairns and Niederlehner (1994), Cockerham (1994), Hoffman et al. (2002), Landis and Ho (1998), Landis and Yu (1994), Lewis (1998), Newman (1998), Yu (200)
Models/Methods	<u>Reviews</u> : Calabrese and Kostecki (1992), U.S. EPA (1990e, 1990f); <u>Specific Methods/Models</u> : Claff (1993), Crane et al. (2001 — time to event models), Erbas-White and San Juan (1993), Pastorok et al. (2001); <u>Soil Damage</u> : USDI (1987a)
Other	<u>Drinking Water</u> : Lowrence (1992), U.S. EPA (1985c, 1990e); <u>Public Health</u> : U.S. EPA (1986–1988, 1986d, 1989d, 1990c, 1990i, 1991d, 1991e)

^a Commonly referred to as the Emergency Planning and Community Right-to-Know Act (EPCRA).

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* See Preface for information on how to obtain documents from CERL and NTIS. See Table 5.3 for number of EPCRA Hotline.

Table 11.11 Index to Major References on Pollution Prevention and Soil and Ground Water Protection Management

Topic	References
Waste Minimization/Pollution Prevention	
Industrial/Commercial	API (1988), Bumble (2000), Cherimisinoff (2001), Engel-Cox and Fowler (1999 — R&D Laboratories), Ghassemi (2001), Higgins (1989 — hazardous waste), Hodge and Popovici (1994 — fertilizer production), Inglesse (1992), Jorgensen (1999), Licit et al. (1991), NJDEPE (1992), Sell (1992), Smallwood (2002 — solvent recovery), Theodore and McGuinn (1992), Theodore et al. (1999), U.S. EPA (1991c, 1991d, 1992d, 1992e, 1993b), Ward et al. (1990), Wise and Trantolo (1994 — wastewater minimization), see also Table 11.6, references on hazardous/industrial wastes handling and treatment in Table 12.7, and references on industrial wastewater treatment in Table 14.9
EPA Series	<u>Guides to Pollution Prevention</u> : U.S. EPA (1990–1993); <u>Waste Minimization Assessments</u> : U.S. EPA (1990–1992); <u>Waste Reduction Activities and Opportunities</u> : U.S. EPA (1992f)
Ground Water Management and Protection	
General Land Use Planning	Ellickson and Tarlock (1981), Freund and Goodman (1968), Getzels and Thurow (1979), Global Cities Project (1993), Hendler (1977), Miller and Wood (1983), Mossa (1987), Robinson (1988), Rusmone (1982), Wilson et al. (1979)
Ground Water Protection	<u>Texts/Reports</u> : Ahmed (1997), Cantor et al. (1987), Conservation Foundation (1987), Greeley-Polhemus Group (1985), Kerns (1977), LeGrand and Rosen (1992), Matthess et al. (1985), Montana Environmental Quality Council (1990), National Research Council (1986), Page (1987), Pojacek (1977), Southern Water Authority (1985), Stroman (1987), U.S. EPA (1984, 1985a, 1987b, 1987g, 1989e, 1991a, 1991b, 1992c), U.S. OTA (1984), WEF (1993/T4.4), Western Michigan University (1988), Zaporozec (1991); <u>Papers</u> : Amsden and Mullen (1990), Flanagan et al. (1991), Henderson (1987), Hodge and Brown (1990), Holmes (1979), LeGrand and Rosen (1992), Lehr (1987), Milde et al. (1983), Pisanelli and Dutram (1990), Tolman et al. (1991), Tripp and Jaffe (1979), Yanggen and Amrhein (1989)
Local Planning Approaches	<u>Texts/Reports</u> : APA (1975), Born et al. (1988), Cross (1991), DiNovo and Jaffe (1984a), Group for the South Fork (1982), Jaffe and DiNovo (1987), MDEP (1991), Michigan Departments of Natural Resources and Public Health (1993), National Research Council (1986), National Rural Water Association (1991), New Hampshire Office of State Planning (1991), Potter (1984), Redlich (1988), Rusmone (1982), University of Oklahoma (1986), U.S. EPA (1989c, 1989d, 1990c), Yanggen and Weberdorfer (1991); <u>Papers</u> : Allee (1986), Blatt (1986), Boody (1990), Dean (1988), DiNovo and Jaffe (1984b), Jaffe (1987), Massey (1984), Oates et al. (1990), Tripp and Jaffe (1979), Yanggen and Amrhein (1989); <u>Ordinances</u> : Minnesota Project (1984), Trefry (1990)
Community Decision Maker/Citizen Guides	Baize and Gilkerson (1992), Born et al. (1987), Central Connecticut Regional Planning Agency (1981), Clark and Cherry (1992), Community Resource Group (1992), Concern (1989), Dean and Wyckoff (1991), Gordon (1984), Hall Associates and Dight (1986), Harrison and Dickinson (1984), Hrezo and Nickinson (1986), Madarchik (1992), Massachusetts Audubon Society (1984–1987), Massachusetts Department of Environmental Quality Engineering (1985), Mullikin (1984), Murphy (undated), North Dakota State Department of Health (1993), Pierce (1992), Raymond (1986), U.S. EPA (1987i, 1990a, 1992a, 1993)
Federal/State Programs	<u>EPA Program Analyses</u> : U.S. EPA (1985b, 1990b, 1992c); <u>State Programs</u> : Booth and Bronson (1983 — New York), Born et al. (1988 — Wisconsin), Environmental Law Institute (1990), Henderson et al. (1985), Leavall (1990 — Ohio), Meccozi (1989 — Wisconsin), National Research Council (1986), NHDES (1991 — NH), Pisanelli and Dutram (1990 — Maine), Raymond (1981), Roy (1988), Stroman (1987 — MA), U.S. EPA (1985c, 1987b, 1987f, 1988a, 1988b, 1989a, 1992b), Walden (1988), Weatherington-Rice and Hottman (1990 — Ohio); <u>Financing</u> : Allee (1986), Shafer et al. (1988), U.S. EPA (1987f, 1987h, 1989a, 1989b, 1992b); <u>WHPA Delineation Methods</u> : Bradbury et al. (1991), Kreitler and Senger (1991), Moore (1993), U.S. EPA (1987a)

Table 11.11 Index to Major References on Pollution Prevention and Soil and Ground Water Protection Management (*Continued*)

Topic	References
Specific Approaches	<u>Best Management Practices</u> : Inglese (1992), Noake (1988), U.S. EPA (1993c); <u>Emergency Planning</u> : New York State Department of Health (1984), U.S. EPA (1985d); <u>Non-Point-Source Pollution Control</u> : Bingham et al. (1993 — urban runoff), Brown et al. (1993 — forest areas), Holmes (1979), ICPRB (1981), Novotny and Chesters (1981), Novotny and Olem (1993), Ritter and Shirmohammadi (2001 — agriculture); <u>Erosion/Sediment Control</u> : APA (1984), Association of Bay Area Governments (1981), Goldman et al. (1986); <u>Agriculture</u> : Baker (1990 — pesticides), Freshwater Foundation (1988–1990), Kemp and Erickson (1989), Lal (1994), Logan et al. (1987), Massey (1984), Stewart (1976), U.S. EPA (1987e, 1988d); <u>Road Salt</u> : Curtis et al. (1986), Greeley-Polhemus Group (1985), NJDEPE (1992); <u>Septic Systems</u> : Lukin (1992), NJDEPE (1992), U.S. EPA (1986a, 1986b, 1987c); <u>Industrial Source Control</u> : See references for waste minimization/pollution prevention above and Table 4.4; <u>Karst</u> : Davis and Quinlin (1991), Fischer et al. (1991), Quinlin et al. (1991), Rubin (1991); <u>Accidental Spills</u> : Yang and Bye (1979a, 1979b); <u>Sole Source Aquifers</u> : U.S. EPA (1987d, 1988c)

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* See Preface for information on how to obtain documents from CERL. Documents available from ODW (U.S. EPA Office of Drinking Water) can be obtained by calling the Safe Drinking Water Hotline (see Table 5.3).

CHAPTER 12

Remediation Planning

Subsurface remediation includes (1) identifying, quantifying, and controlling contaminant source(s); (2) considering cleanup levels required for each medium (air, soil, and ground water) to protect human health and the environment; and (3) selecting treatment technologies based on information obtained concerning source(s) and cleanup levels. The challenge is to effectively relate site characterization activities to selecting the most appropriate remediation technologies for contaminated soils and ground water at hazardous waste sites. Effectively relating these activities with technology selection improves the efficiency, purpose, and results of both site characterization and remediation technique selection. This chapter addresses specific subsurface physical, chemical, and biological processes that have been discussed in Part I within the context of (1) site characterization requirements, (2) evaluation and selection of remediation techniques and treatment trains utilizing several techniques, and (3) design of monitoring programs. Specific soil and aquifer remediation techniques are addressed in more detail in Chapters 13 (Remediation of Contaminated Soils) and 14 (Remediation of Contaminated Ground Water).

12.1 CONCEPTUAL APPROACH TO SOIL AND GROUND WATER REMEDIATION

This chapter uses the *chemical mass balance* approach as the conceptual framework for soil and ground-water remediation technique evaluation, selection, and monitoring. The concept of a chemical mass balance is familiar to professionals trained in the physical or life sciences or in engineering. It provides a rational and fundamental basis for asking specific questions and obtaining specific information that is necessary for determining fate and behavior, for evaluating and selecting treatment options, and for monitoring treatment effectiveness at both the laboratory scale and field scale. A mass balance approach also meets the goal of obtaining quantitative accuracy about the amount of contaminants initially present at an uncontrolled site. While a mass balance, or materials balance, is routinely conducted on aboveground treatment processes (Bailey and Ollis, 1986/T12.7; Benefield et al., 1982/T14.9; Corbitt, 1989/T12.7) and for ground-water processes (Willis and Yeh, 1987/T14.9; Wilson et al., 1989/T12.7), a mass balance approach has generally not been applied to the soil environment or to the subsurface/surface system to link characterization activities and treatment technology selection. The information needed to construct a mass balance for contamination at a site simultaneously addresses site characterization and remediation evaluation and selection.

The mass balance conceptual approach for the soil and ground-water subsurface environment at a contaminated site is illustrated in [Figure 12.1](#). The contaminated subsurface is a system

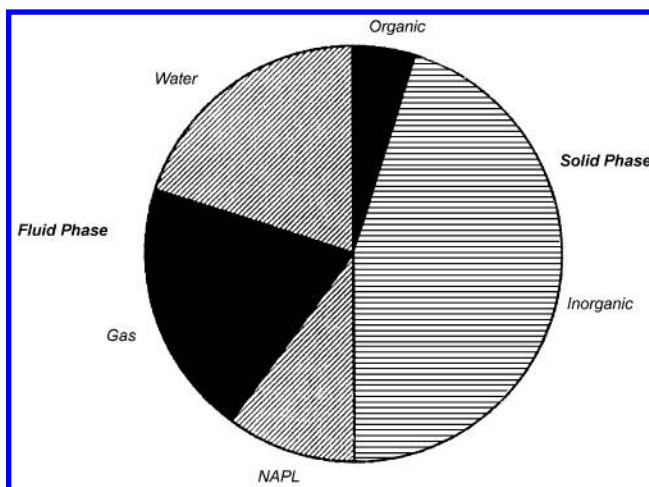


Figure 12.1 Mass balance conceptual framework for the soil and ground-water subsurface environment at a contaminated site (Sims and Sims, 1991a).

generally consisting of two phases (solid and fluid) and five compartments (gas, an inorganic mineral solid compartment, an organic matter solid compartment, water, and oil (NAPL)) (Sims et al., 1989/T13.9). Generally NAPLs are subdivided into two classes: those that are lighter than water (LNAPLs), and those with a density greater than water (DNAPLs) — Section 4.4.3. LNAPLs include hydrocarbon fuels, such as gasoline, heating oil, kerosene, jet fuel, and aviation gas. DNAPLs include chlorinated hydrocarbons, such as 1,1,1-trichloroethane, carbon tetrachloride, chlorophenols, chlorobenzenes, tetrachloroethylene, and polychlorinated biphenols (PCBs).

Specific subsurface processes concerning water movement, sampling, sorption and reaction, and degradation are discussed in Chapters 3 and 4. The processes and terminology described in the previous chapters will be used in this chapter for the discussion of the components of a mass balance and the mass balance approach to evaluation and selection of soil remediation techniques.

Interphase transfer potential for waste constituents among oil (waste or NAPL), water, air, and solid (organic and inorganic) phases of a subsurface system is affected by the relative affinity of waste constituents for each phase shown in Figure 12.1, and may be quantified through calculation of distribution coefficients (Loehr, 1989/T13.9; Sims et al., 1988/T13.9; U.S. EPA, 1986a/T12.7). Distribution coefficients are calculated as the ratio of the concentration of a chemical in the soil (or aquifer materials), oil, or gas phases to the concentration of a chemical in the water phase. A waste chemical, depending on its tendency to be associated with each phase, will distribute itself among the phases, and can be quantified in terms of distribution coefficients. Distribution coefficients are available for a variety of chemicals and can be expressed as ratios of the concentrations of a chemical between two phases in the subsurface:

K_d = concentration in solid phase/concentration in aqueous phase

K_o = concentration in oil phase/concentration in aqueous phase

K_h = concentration in air phase/concentration in aqueous phase

When distribution coefficients are not available, they can be estimated using structure–activity relationships (SARs) or can be determined in laboratory tests (Sims et al., 1988/T13.9).

Distribution coefficients have been used most successfully with organic chemicals. However, since metals distribute among the phases of the subsurface systems described previously, distribution coefficients also may be used, along with multiphase metal speciation information (Sims et al., 1984/T13.9), to evaluate metal distribution in a contaminated subsurface system.

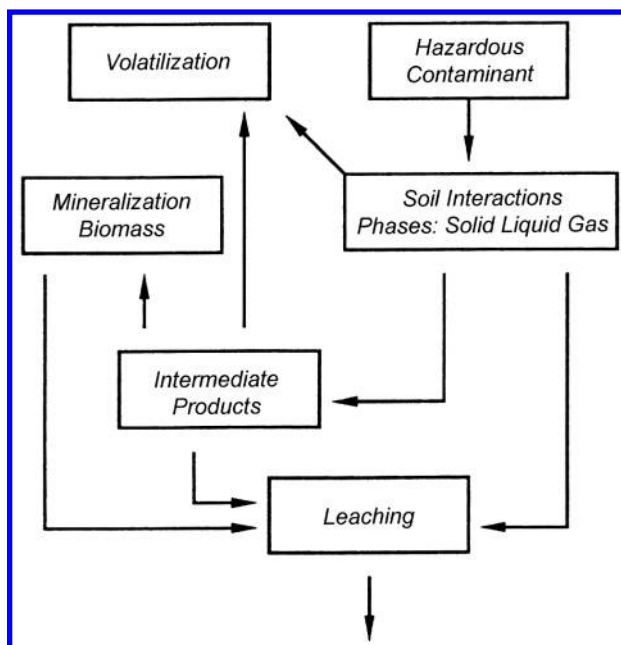


Figure 12.2 Interphase transfer potential of chemicals in the subsurface (Sims and Sims, 1991a).

Knowledge of migration and distribution of chemicals and chemical intermediates among the phases and compartments of a contaminated subsurface system (illustrated in Figure 12.2) provides fundamental information about the fate and behavior of contaminants, which can be used for selecting and evaluating subsurface remedial techniques. Retardation of the downward transport (leaching potential) and upward transport (volatilization potential) is referred to as immobilization of waste constituents, and has been related to the subsurface organic matter content, especially for hydrophobic chemicals (Nkedi-Kizza et al., 1983), soil moisture, and presence and concentration of organic solvents (Mahmood and Sims, 1986; Rao et al., 1985).¹

In summary, the subsurface processes described above, combined with information about the movement of fluids (gases, aqueous phase, and pure product flow) in the unsaturated and saturated zones, provide the inputs into the chemical mass balance that can be used for (1) characterizing a site, (2) assessing the problem of mobility, (3) evaluating treatment techniques, and (4) identifying chemicals in specific phases for monitoring treatment effectiveness.

12.2 METHODOLOGY

Remediation of contaminated soil and ground water consists of four elements: (1) characterization, (2) assessment of the problem, (3) treatment (train) selection, and (4) monitoring treatment performance (Figure 12.3). The first element involves characterization in the context of waste–subsurface–site interactions to address the question “Where is the contamination and in what form(s) does it exist?” The second element, assessment of the problem, utilizes subsurface fate and behavior information to address the question “Where is the contamination going under the influence of natural processes?” The problem can be defined in the context of mobility vs. degradation for chemicals at

¹ Mahmood, R.J. and R.C. Sims. 1986. Mobility of Organics in Land Treatment Systems. *Journal of Environmental Engineering (ASCE)* 112:236–245. Nkedi-Kizza, P., P.S.C. Rao, and J.W. Johnson. 1983. Adsorption of Diuron and 2,4,5-T on Soil Particle Separates. *Journal of Environmental Quality* 12:195–197. Rao, P.S.C., A.G. Hornsby, D.P. Kilcrease, and P. Nkedi-Kizza. 1985. Sorption and Transport of Hydrophobic Organic Chemicals in Aqueous and Mixed Solvent Systems: Model Development and Preliminary Evaluation. *Journal of Environmental Quality* 14:376–383.

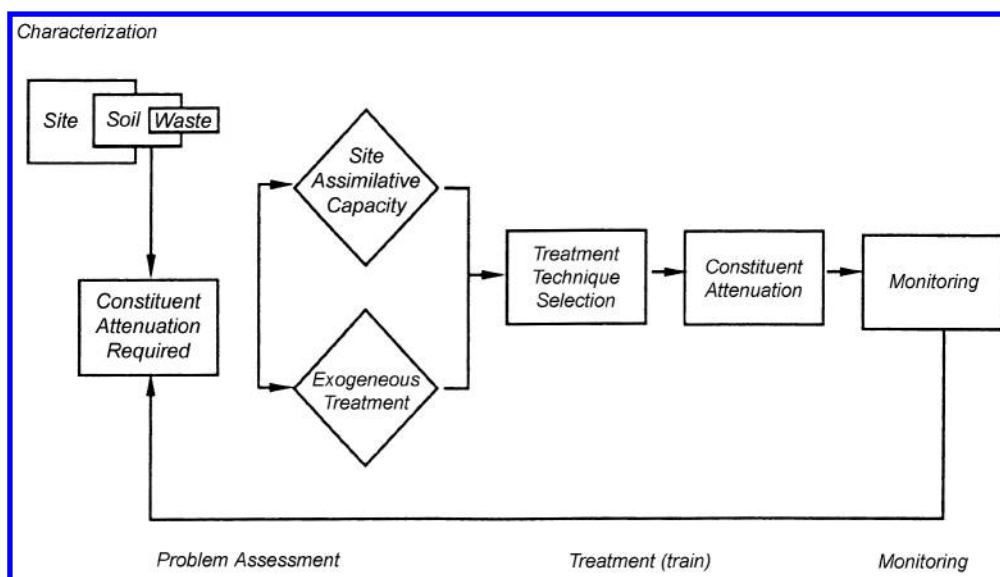


Figure 12.3 Methodology using mass balance approach for integrating data collection activities at a contaminated site (Sims and Sims, 1991a).

a site. Using mathematical models or other tools, the chemicals can be ranked in order of their relative tendencies to leach, volatilize, move in an NAPL phase, and remain in place under site-specific conditions. Containment and treatment options then can be selected that are chemical specific and that address specific escape and attenuation pathways (third element). Therefore, treatment trains can be selected to address specific waste phases at specific times during remediation (volatile, leachate, solid phase, and pure product), with the selection based upon results of a mass balance evaluation through time to identify the fate of each waste phase. Finally, monitoring programs can be designed for specific chemicals in specific phases in the subsurface at specific times (fourth element).

The approach for using the methodology described above consists of applying a mass balance for each element of the methodology. This approach assists in the collection of specific information that is transferable among all four elements of the methodology, and also addresses the technical issues of soil remediation within the context of regulatory goals.

12.2.1 Site Characterization

Identifying waste sources by subsurface phases, i.e., identification and amount (if possible) of waste constituents associated with solid and fluid phases (Figure 12.1), allows assessment of the magnitude (mass) and physical form(s) of waste that must be treated. This assessment comprises the first step in the mass balance characterization of waste sources at a site.

Wastewater historically has been characterized and subsequently treated in terms of its interaction and potential impact on the assimilative capacity of surface water receiver systems, generally rivers or lakes (e.g., requiring measurement of characteristics such as oxygen-demanding substances, nutrients, and levels of substances toxic to aquatic organisms). However, a waste characterization program at a contaminated site addresses the vadose zone and ground water, in addition to surface water, as the receiver systems (e.g., requiring measurement of characteristics that reflect individual chemical mobility and destruction in the subsurface environment and those that affect human health, as well as characteristics that affect environmental toxicity — see Figure 11.8). Also, it describes the behavioral interaction of waste chemicals in each surface and subsurface phase. Thus, hazardous waste is more appropriately characterized in terms of the interaction and potential impact on the subsurface assimilative capacity.

Table 12.1 Subsurface-Based Waste Characterization

Chemical Class
Acid
Base
Polar neutral
Nonpolar neutral
Inorganic
Chemical Properties
Molecular weight
Melting point
Specific gravity
Structure
Water solubility
Chemical Reactivity
Oxidation
Reduction
Hydrolysis
Precipitation
Polymerization
Soil Sorption Parameters (Section 4.5.2)
Freundlich sorption constants (K , a)
Sorption based on organic carbon content (K_{oc})
Octanol–water partition coefficient (K_{ow})
Soil Degradation Parameters
Half-life ($t_{1/2}$)
Rate constant (first order — Section 3.1.1)
Relative biodegradability (Section 3.5.4)
Soil Volatilization Parameters
Air–water partition coefficient (K_w)
Vapor pressure
Henry's law constant
Sorption based on organic carbon content (K_{oc})
Water solubility
Soil Contamination Parameters
Concentration in soil
Depth of contamination
Date of contamination

Source: Sims and Sims (1991a), after Sims et al. (1984).

Specific site characteristics important for describing and assessing the environmental behavior and fate of organic constituents in the soil and subsurface are listed in Table 12.1. For each chemical, or chemical class, required information includes (1) characteristics related to potential leaching (e.g., water solubility, octanol–water partition coefficient, solid sorption coefficient); (2) characteristics related to potential volatilization (e.g., vapor pressure, relative volatilization index); (3) characteristics related to potential degradation (e.g., half-life, degradation rate, degradability index); and (4) characteristics related to chemical reactivity (e.g., hydrolysis half-life, soil redox potential) (Sims et al., 1984/T13.9). The information presented in Table 12.1 also is used to assess problem(s) concerning migration potential at a site and to evaluate and select containment and treatment management options. Table 12.2 identifies site characterization data needs for major methods used to stabilize and remediate contaminated sites.

If the distribution of waste chemicals among phases that comprise the soil and subsurface at a site is determined, then potential pathways of transport, or escape, from a site can be indicated. Therefore, exposure pathways for human health and the environment may be evaluated; i.e., risk assessment can be made. Through a determination of subsurface flow conditions as part of site characterization activities (aqueous, gas, and pure product flow in the vadose zone and aqueous plume and pure product movement in the saturated zone), the mass of material moving through a site and potential movement off-site can be assessed:

Table 12.2 Data Needs for Major Stabilization and Remediation Methods (Bartenfelder et al., 1992)

	Drains and Trenches	Capping	Slurry Wall	Runoff/ Runon Control	Gas Venting	Solidification	<i>In Situ</i> Soil Flushing	Bioremediation	Vacuum Extraction	Pump and Treat
Depth to water table	■	□	■	—	□	■	□	□	■	■
Surface water/ground water relationship	■	—	□	—	—	—	□	—	—	■
Ground-water flow rates and direction	■	—	■	—	—	—	□	—	—	■
Seasonal changes in ground-water elevation	■	□	—	—	□	□	□	□	□	■
Hydraulic conductivity/permeability	■	■	■	—	■	—	■	■	■	■
Climate/precipitation	■	■	—	■	—	■	—	■	■	—
Contaminant characteristics	■	□	■	—	■	■	■	■	■	■
Contaminant concentration	■	—	■	—	■	■	■	■	■	■
Extent of contamination	■	■	■	—	■	■	■	■	■	■
Types, thicknesses, and extents of saturated and unsaturated subsurface materials	■	—	■	—	□	□	■	■	■	■
Soil characteristics	□	—	■	■	■	—	■	■	■	■
Soil water content	—	—	—	—	■	■	—	■	■	—
Depth of air permeable zone	—	—	—	—	■	—	—	■	■	—
Topography	—	■	■	■	—	—	—	—	—	—
Depth of aquitard	□	—	■	—	—	—	□	—	—	■

Note: ■, high priority; □, medium priority; —, low priority.

$$\text{Concentration (mass/volume)} \times \text{rate of flow (volume/time)} = \text{mass flow at site (mass/time)}$$

This information is combined with additional information, discussed in the next section, that is needed to assess the problem(s) with respect to treatment technique selection.

12.2.2 Assessment of Problem

Assessment of the contamination involves organizing the information obtained from site characterization activities to evaluate the transport and degradation behavior of each chemical of concern at a site under consideration. Specifically, the rate of transport can be compared with the rate of degradation to determine if transport is significant relative to degradation. This approach to problem(s) assessment will allow chemicals to be prioritized individually according to (1) magnitude and rate of transport (escape) from a site, (2) persistence, and (3) pathway(s) of migration from a site. Treatment technique evaluation and selection then can be based upon specific combinations of chemical and physical phase-migration pathway(s).

Interfacing subsurface-based behavioral characteristics of specific contaminants (Table 12.1) with specific site and subsurface properties allows an assessment of the problem(s) related to contamination of other media (due to mobility), including the ground water under the contaminated area, the atmosphere over the site or at the site boundaries, surface waters, and persistence of chemicals at a site. Pathways of movement and potential mechanisms of removal of contaminants at a specific site are illustrated in Figure 12.2. This element of the methodology functions to identify chemicals that will (1) migrate upward (volatilization), (2) migrate downward (leaching), (3) migrate laterally (aqueous plume and pure product), (4) degrade, and (5) remain at the site as persistent chemicals. By ranking the chemicals in the order in which they migrate or persist, chemicals can be prioritized with regard to urgency for treatment and monitoring.

Waste characteristics identified in Table 12.1, including potential sorption, degradation, and volatilization at a site, can be determined in laboratory mass balance tests, using waste–soil mixtures from a site. These characteristics can be used to evaluate the fate of the waste at the site, and to generate specific data that can be used to develop treatment approaches. Figure 12.4 illustrates a laboratory flask apparatus that can be used to develop a chemical mass balance by measuring the interphase transfer potential of chemicals as well as the degradation potential at a site.

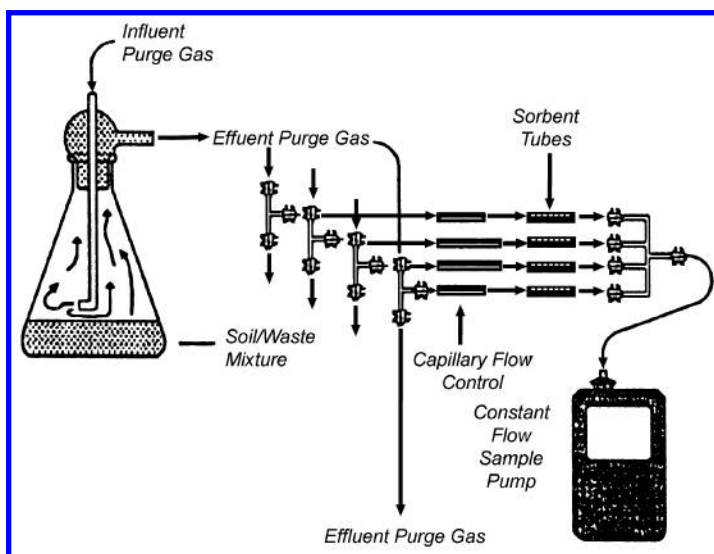


Figure 12.4 Laboratory flask apparatus used for mass balance measurements (Sims and Sims, 1991a, after Park et al., 1990).

The contaminated material is placed in a flask, which is then closed and incubated under controlled conditions for a period of time. During the incubation period, air is drawn through the flask and then through a sorbent material. Volatilized materials are collected by the sorbent and are measured to estimate volatilization loss of the constituents of interest. At the end of the incubation period, a portion of the contaminated soil is treated with an extracting solution to determine the extent of loss of the constituents in the soil matrix. This loss can be attributed to degradation and possible immobilization in the soil materials. It is necessary to select an appropriate extracting solution and procedure to maximize constituent recovery from a soil–waste mixture (Coover et al., 1987).² Another portion of the soil is leached with water to determine leaching potential of the remaining constituents. Abiotic and biological processes involved in removal of the parent compound are evaluated by comparing microbially active soil–waste mixtures with mixtures that have been treated with a microbial poison, e.g., mercuric chloride or propylene oxide. Samples generated from the different phases of the system in microcosm mass balance studies identified above can be analyzed for intermediate degradation products and used in bioassay studies to provide information concerning transformation and detoxification processes.

The use of a procedure incorporating features illustrated by the use of this microcosm (Figure 12.4) is crucial to obtain a materials balance of waste constituents in the subsurface system. Examples of such protocols may be found in EPA guidance documents and research reports (Loehr, 1989/T13.9; Sims et al., 1988/T13.9; EPA, 1986a/T12.7; Park et al., 1990).³ Contaminated materials also can be spiked with radiolabeled chemicals; tracking the fate of the chemicals as they move through the multiple phases of the soil system also provides a materials mass balance.

The mass balance approach identified above usually represents optimum conditions with respect to mixing, contact of solid materials with waste constituents, and homogeneous conditions throughout the laboratory microcosm; therefore, it does not incorporate site heterogeneity in the evaluation. This aspect must be defined during site characterization activities and evaluated with regard to potential effect on fate and behavior regarding migration and persistence at the site (problem assessment).

In addition to the laboratory tests described, bench-scale reactors, pilot-scale reactors, and field-scale plots may be used to generate mass balance information for problem assessment. The set of experimental conditions (e.g., temperature, moisture, waste concentration) under which the studies were conducted and experimental results should be presented.

Information from the performance of site characterization and experimental mass balance studies may be integrated with the use of comprehensive mathematical modeling to aid in problem assessment. In general, models are used to analyze the behavior of an environmental system under both current (or past) and anticipated (or future) conditions (Donigian and Rao, 1986a/T10.6). A mathematical model provides a tool for (1) integrating degradation and partitioning processes with site-, soil-, and waste-specific characterization; (2) simulating the behavior of waste constituents in a contaminated soil; and (3) predicting the pathways of migration through the contaminated area, and therefore pathways of exposure to humans and the environment. Diguilio and Suffet (1988)⁴ and Weaver et al. (1989/T10.6) have presented guidance on the selection of appropriate subsurface zone models for site-specific applications, focusing on recognition of limitations of process descriptions of models and difficulties in obtaining input parameters required by these process descriptions.

The Regulatory and Investigative Treatment Zone (RITZ) model is an example of a vadose zone model that has been used to describe the potential fate and behavior of organic constituents in a contaminated soil system (Nofziger and Williams, 1988/TE.2). The RITZ model is based on

² Coover, M.P., R.C. Sims, and W.J. Doucette. 1987. Extraction of Polycyclic Aromatic Hydrocarbons from Spiked Soil. *Journal of the Association of Official Analytical Chemists* 70:1018–1020.

³ Park, K.S., R.C. Sims, R.R. Dupont, W.J. Doucette, and J.E. Matthews. 1990. Fate of PAH Compounds in Two Soil Types: Influence of Volatilization, Abiotic Loss and Biological Activity. *Environ. Toxicol. Chem.* 9:187–195.

⁴ Diguilio, D.C. and I.H. Suffet. 1988. Effects of Physical, Chemical, and Biological Variability in Modeling Organic Contaminant Migration through Soil. In: *Superfund '88, Hazardous Materials Control Research Institute*, Silver Spring, MD, pp. 132–137.

an approach developed by Jury et al. (1983).⁵ An expanded version of RITZ, the Vadose Zone Interactive Processes (VIP) model, incorporates predictive capabilities for the dynamic behavior of organic constituents in unsaturated soil systems under conditions of variable precipitation, temperature, and waste concentrations (McLean et al., 1988⁶; Stevens et al., 1993/TE.2; Symons et al., 1988⁷). Both the RITZ and VIP models simulate vadose zone processes, including volatilization, degradation, sorption/desorption, advection, and dispersion (Grenney et al., 1987).⁸

For example, the VIP model was used to evaluate the relative tendencies for a group of pesticides to volatilize and leach under specific waste-soil conditions (McLean et al., 1988 — footnote 6). Information input into the model included half-life (measured in laboratory tests), distribution coefficients — K_d , K_h , and K_o (calculated) — soil texture and moisture (measured), and site-specific climatic data (rainfall and temperature). The ranking of pesticides provided by the model indicated that the tendency of the pesticides to volatilize was not similar to their tendency to leach. Such information can be used to assess which chemicals are likely to volatilize first, which chemicals are likely to leach first, and which chemicals are persistent under site-specific conditions. In addition to assisting in the problem assessment step of the methodology, mathematical models also can be used to design studies for evaluation and selection of treatment options for these chemicals, as well as to design monitoring strategies (i.e., which chemicals to monitor in which media).

Ground-water flow and transport models can also be used as part of the problem assessment (Sections 10.3 and 10.4). Table 10.1 identifies types of modeling that may be useful for design of corrective action measures. Some ground-water models are specifically designed for evaluating contaminated sites. For example, a numerical model, BIOPLUME, was developed to simulate oxygen-limited biodegradation in ground-water environments. BIOPLUME simulates advection, dispersion, and retardation processes as well as the reaction between oxygen and the contaminants under steady, uniform flow (Rifai et al., 1988; Bedient et al., 1989/TE.2). BIOPLUME has been applied to an aviation gasoline spill site at Traverse City, MI. Model predictions for the rates of mass loss closely matched calculated rates from field data. Table E.2 provides an index to PC-based ground water and vadose zone flow and contaminant transport models.

12.2.3 Interim Corrective Action

Depending on the degree of hazard presented by contaminants at a site, interim corrective action measures may be required before site characterization and problem assessment provide enough data for identification of the best permanent treatment approach. Table 12.3 identifies examples of interim measures for a variety of situations where immediate action at a site is justified. The extent and aggressiveness of interim measures will be determined by the degree of risk posed by the contamination (Section 11.4).

12.2.4 Treatment Approaches

Information obtained from an integrated assessment (modeling) of the problem (migration and persistence), based upon a thorough characterization of waste–soil–site interactions, can be used to select treatment approaches for further evaluation with respect to technical and cost-effectiveness factors. Results of characterization and assessment efforts can aid in the identification of constituents that will require treatment in the following phases: (1) air (volatile) phase, (2) leachate phase, and

⁵ Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behavior Assessment Model for Trace Organics in Soil: Model Description. *Journal of Environmental Quality* 12:558–564.

⁶ McLean, J.E., R.C. Sims, W.J. Doucette, C.L. Caupp, and W.J. Grenney. 1988. Evaluation of Mobility of Pesticides in Soil using U.S. EPA Methodology. *Journal of Environmental Engineering (ASCE)* 114:689–703.

⁷ Symons, B.D., R.C. Sims, and W.J. Grenney. 1988. Fate and Transport of Organics in Soil: Model Predictions and Experimental Results. *Journal Water Pollution Control Federation* 60:1684–1693.

⁸ Grenney, W.J., C.L. Caupp, R.C. Sims, and T.E. Short. 1987. A Mathematical Model for the Fate of Hazardous Substances in Soil: Model Description and Experimental Results. *Hazardous Wastes & Hazardous Materials* 4:223–239.

Table 12.3 Examples of Interim Measures for Corrective Action at Contaminated Sites

Unit	Possible Interim Measures
Containers	<ul style="list-style-type: none"> • Overpack/redrum • Construct storage area; move to new storage area • Segregation • Sampling and analysis • Treatment, storage, and disposal • Temporary cover
Tanks	<ul style="list-style-type: none"> • Overflow/secondary containment • Leak detection/repair • Partial or complete removal
Surface Impoundments	<ul style="list-style-type: none"> • Reduce head • Remove free liquids and highly mobile wastes • Stabilize/repair sidewalls, dikes, or liner(s) • Temporary cover • Runoff/run-on control (diversion or collection devices) • Sampling and analysis • Interim ground-water measures (see below)
Landfills	<ul style="list-style-type: none"> • Runoff/run-on control (diversion or collection devices) • Reduce head on liner and in leachate collection system • Inspect leachate collection/removal system or French drain • Repair leachate collection/removal system or French drain • Temporary cap/cover • Waste removal to more secure location • Interim ground water measures (see below)
Waste Piles	<ul style="list-style-type: none"> • Runoff/run-on control (diversion or collection devices) • Temporary cap/cover • Waste removal to more secure location • Interim ground water measures (see below)
Soils	<ul style="list-style-type: none"> • Sampling and analysis • Removal to more secure location • Temporary cap/cover
Ground Water	<ul style="list-style-type: none"> • Delineation/verification of gross contamination • Sampling and analysis • Interceptor trench/sump/subsurface drain • Pump and treat • <i>In situ</i> treatment • Temporary cap/cover
Surface Water Releases (Point and Nonpoint)	<ul style="list-style-type: none"> • Overflow/underflow dams • Filter fences • Runoff/run-on control (diversion or collection devices) • Regrading/revegetation • Sampling and analysis of surface water/sediment/point source
Gas Migration Control	<ul style="list-style-type: none"> • Barriers • Collection and treatment • Monitoring
Particulate Emissions	<ul style="list-style-type: none"> • Truck wash (decontamination unit) • Revegetation • Application of dust suppressant
Other Actions	<ul style="list-style-type: none"> • Fencing to prevent direct contact • Sampling off-site areas • Alternate water supply for contaminated drinking water • Temporary relocation of exposed population • Temporary or permanent injunction • Suspend/revoke authorization to operate under interim status

Source: Adapted from U.S. EPA (1988c).

(3) solid (soil) phase. This approach allows evaluation and comparison of different treatment systems identified previously (*in situ* and prepared bed). Specifically, if treatment is required, the information is used to (1) determine containment requirements to prevent contamination of off-site receiver systems; (2) develop techniques to maximize mass transfer of chemicals affecting a process (e.g., affecting microbial activity through addition of mineral nutrients, oxygen, additional energy sources, pH control products, or removal of toxic products in order to enhance bioremediation); and (3) design a cost-effective and efficient monitoring program to evaluate effectiveness of treatment.

Containment Requirements. If the major pathway of transport is volatilization, containment and treatment to control volatilization are required. An inflatable plastic dome erected over a contaminated site is a containment method that has been used to control escape of volatile constituents at hazardous waste sites (St. John and Sikes, 1988).⁹ Volatiles are drawn from the dome through a conduit and treated in an aboveground treatment system. If leaching has been identified as an important factor, control of soil water movement should be implemented. For example, if contaminated materials are expected to leach downward from the site, run-on and runoff controls can be implemented, or the contaminated materials can be temporarily removed from the site and a plastic or clay liner can be placed under the site (Lynch and Genes, 1989; Ross et al., 1988).¹⁰ When downward as well as upward migration are significant, both volatilization and leaching containment systems can be installed. Some hydrophobic chemicals do not tend to volatilize or leach but are persistent within the soil solid phase; therefore, containment efforts may not be required. With regard to the saturated zone, containment is generally accomplished by physical barriers (e.g., slurry walls, sheet pilings, grout curtains) or hydraulic barriers (e.g., pumping systems, French drains). Section 14.3 addresses containment of contaminants in more detail.

Maximizing Chemical Mass Transfer. An area of significant research concerns delivery and recovery technologies for maximizing mass transfer of chemicals that affect the rate and extent of treatment. Murdoch et al. (1988/T12.7) discussed delivery and recovery technologies, many of which are derived from the petroleum and mining industries. While a liquid phase is usually employed for delivery of chemicals, some technologies utilize vapor and solid phases for delivery. Principal recovery technologies involve hydraulic, thermal, and chemical systems. Delivery and recovery techniques are important in influencing the success of technologies, including bioremediation, vapor extraction, and solidification/stabilization. Specific delivery and recovery systems for *in situ* treatment systems identified by EPA include hydraulic fracturing, radial well drilling, ultrasonic methods, kerfing, jet-induced slurry methods, carbon dioxide injection, hot brine injection, and cyclic pumping (Chambers et al., 1990/T13.9).

12.2.5 Monitoring Program

A mass balance approach to monitoring, the fourth element in the methodology (Figure 12.3), can be performed at laboratory, pilot, and field scales. Monitoring efforts can be focused on the appropriate environmental phase to evaluate treatment effectiveness for specific chemicals. If a comprehensive and thorough evaluation of a specific contaminated system has been conducted, not all chemicals may need to be monitored in each phase. Specific chemicals will be associated with specific phases; therefore, a monitoring plan can be designed that is chemical and phase specific. This approach also focuses analytical efforts so that methods of development are chemical and phase specific.

⁹ St. John, W.D. and D.J. Sikes. 1988. Complex Industrial Waste Sites. In: Environmental Biotechnology — Reducing Risks from Environmental Chemicals through Biotechnology, G.S. Omenn, Ed., Plenum Press, New York, pp. 237–252.

¹⁰ Lynch, J. and B.R. Genes. 1989. Land Treatment of Hydrocarbon Contaminated Soils. In: Petroleum Contaminated Soils, Vol. 1: Remediation Techniques, Environmental Fate, and Risk Assessment, P.T. Kostecki and E.J. Calabrese (Eds.), Lewis Publishers, Chelsea, MI, pp. 163–174. Ross, D., T.P. Marziarz, and A.L. Bourquin. 1988. Bioremediation of Hazardous Waste Sites in the USA: Case Histories, In: Superfund '88, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 395–397.

The level of contamination associated with a particular treatment technology requires monitoring. In addition, the treatment system components, including delivery and recovery systems, maintenance, and structures such as infiltration galleries, must be monitored.

12.2.6 Health and Safety Considerations

A health and safety plan should be part of the sampling plan. The past history of the site and the chemicals used on the site determine the level of personal protection required. The appropriate level of protection should be determined prior to initial entry to the site and changed as more information is obtained. The *Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities* (NIOSH/OSHA/USCG/EPA, 1985/T12.7) describes the levels of personal protective clothing and equipment and their applications. [Table 12.7](#) identifies other major references addressing health and safety aspects of investigations and remediation of contaminated sites.

12.3 SELECTION OF TREATMENT METHODS

[Table 12.4](#) provides a matrix of general remedial technology categories for 18 specific site problems, and also identifies sections in U.S. EPA (1985) where more detailed information can be obtained about each category. The number of possible treatment methods for contaminated soil and ground-water borders on being bewildering. [Table 12.5](#) provides a matrix of major types of organic and inorganic contaminants and 16 major categories of treatment technologies for soils and sludges that can be used as a guide for initial screening of potential technologies for a particular situation. [Table 13.1](#) through [Table 13.4](#) and [Table 14.3](#) through [Table 14.7](#) provide more detailed information on specific types of soil and ground-water treatment techniques, respectively.

12.3.1 Utility of Mathematical Models

A critical and cost-effective use of modeling in treatment (train) selection and evaluation is for analysis of proposed or alternative future conditions; i.e., the model is used as a management or decision-making tool to help answer “what if” questions (Donigian and Rao, 1986a/T10.6). Models also may be used to approximate and estimate the rates and extent of treatment that may be expected at the field scale under varying conditions. Attempting to answer such questions through data collection programs would be expensive and practically impossible in many situations. For example, information can be generated to evaluate the effects of using different approaches for enhancing microbial activity and for accelerating biodegradation and detoxification of the contaminated area by altering environmental conditions that affect microbial activity. Therefore, modeling may be used to assist in the design of treatability studies for considering and evaluating the application of different treatment technologies, and therefore to assist in focusing available resources (time and money). [Section 12.2.2](#) (Assessment of Problem) gives some examples of mathematical models for vadose zone and ground-water remediation, and Chapter 10 addresses modeling in more detail.

12.3.2 Treatability Studies

Treatability studies can be used for evaluating and comparing rate and extent of remediation among several technologies and also to provide specific information about the potential application of treatment technologies at the field scale. Treatability studies can be conducted in laboratory microcosms or bench-scale reactors, pilot-scale facilities, or the field. Laboratory treatability studies are generally screening studies used to (1) establish the validity of a technology, (2) generate data that can be used as indicators of potential to meet performance goals, and (3) identify parameters for investigation during bench- or pilot-scale testing. Laboratory treatability studies are generally

Table 12.4 Matrix of Remedial Technology Categories for Specific Site Problems (U.S. EPA, 1985)

Site Problem	Remedial Technology Categories									
	Surface Water Controls (see Section 3)	Air Pollution Controls (see Section 4)	Leachate and Groundwater Controls (see Section 5)	Gas Migration Control (see Section 6)	Waste and Soil Excavation and Removal and Land Disposal (see Section 7)	Contaminated Sediments Removal and Containment (see Section 8)	<i>In Situ</i> Treatment (see Section 9)	Direct Waste Treatment (see Section 10)	Contaminated Water Supply and Sewer Line Controls (see Section 11)	
Volatilization of chemicals into air		●								
Hazardous particulates released to atmosphere		●								
Dust generation by heavy construction or other site activities		●								
Contaminated site run-off	●									
Erosion of surface due to wind or water	●									
Surface seepage of leachate	●									
Flood hazard or contact of surface water body with wastes	●									
Leechate migrating vertically or horizontally			●				●			
High water table which may result in groundwater contamination or interfere with other remedial technologies			●							
Precipitation infiltrating into site to form leachate	●		●							
Evidence of methane or toxic gases migrating laterally underground				●						
On-site waste materials in non-disposed form: drums, lagooned waste, wastepiles					●		●	●		
Contaminated surface water, groundwater or other aqueous or liquid waste					●		●	●		
Contaminated soils					●		●	●		
Toxic and/or hazardous gases which have been collected								●		
Contaminated stream banks and sediments					●	●		●		
Drinking water distribution system contamination										●
Contaminated sewer lines										●

not appropriate for generating design or cost data (U.S. EPA, 1989b/T12.7). Pilot-scale testing is conducted to generate information on quantitative performance, cost, and design information. Three categories of treatability testing and associated descriptions are included in [Table 12.6](#).

Treatability study results are commonly used to provide information on rates and extent of treatment of hazardous organic constituents when mass transfer rates of potential limiting substances are not limiting the treatment. Treatability studies also usually represent optimum conditions with respect to mixing, contact of soil solid materials with waste constituents and with microorganisms, and homogeneous conditions throughout the microcosm. Therefore, treatability studies provide information concerning potential levels of treatment. Rates and extent of remediation in a prepared bed or *in situ* system are generally limited by accessibility and rate of mass transfer of chemical

Table 12.5 Treatment Technology Screening Guide for Different Contaminants in Soils and Sludges (U.S. EPA, 1989c)

[illegible]

Note: ●, demonstrated effectiveness; ◐, potential effectiveness; ○, no effectiveness; X, potential adverse impacts to process or environment.

* Do not use this matrix table alone. Please refer to the cite appendixes for guidance.

substances to the contaminated soil and removal of inhibitory microbial degradation products (Symons and Sims, 1988).¹¹

Information from mass balance treatability studies, including laboratory screening-, bench-, and pilot-scale studies, is combined with information about site and waste characteristics to determine

¹¹ Symons, B.D. and R.C. Sims. 1988. Assessing Detoxification of a Complex Hazardous Waste Using the Microtox™ Bioassay. Archives of Environmental Contamination and Toxicology 17:497-505.

Table 12.6 General Comparison of Laboratory Screening, Bench-Scale Testing, and Pilot-Scale Testing

	Laboratory Screening	Bench-Scale Testing	Pilot-Scale Testing
Type of data generated	Qualitative	Quantitative	Quantitative
Critical parameters	Several	Few	Few
No. of replicates	Single/duplicate	Duplicate/triplicate	Triplicate or more
Study size	Jar tests or beaker studies	Bench-top (some larger)	Pilot plant (on-site or off-site)
Usual process type	Batch	Batch or continuous	Batch or continuous
Waste stream volume	Small	Medium	Large
Time required	Hours/day	Days/week	Weeks/month
Cost (\$1000)	10–50	50–250	250–1000

Source: Sims and Sims (1991a), after U.S. EPA (1989d).

applications and limitations of each technology. Information obtained from treatability studies should be focused on identifying ultimate limitations to the use of a remediation technology at a specific site. Limitations are usually related to (1) time required for cleanup, (2) level of cleanup attainable, and (3) cost of cleanup (Sims et al., 1989/T13.9). Table 12.7 identifies other major references on methods for assessing treatability of contaminated materials.

12.3.3 Treatment Trains

The use of treatment trains also is important to consider in an engineering approach for using treatment techniques for subsurface site remediation. For example, vacuum extraction is known to be applicable to unsaturated sites characterized by permeable materials containing volatile chemicals. Vacuum extraction also can be used for the degradation of more semivolatile chemicals. This degradation is accomplished by providing a source of oxygen (air) to the subsurface environment microorganisms where anoxic conditions exist due to relative slow replenishment of oxygen through atmospheric diffusion. This is an example of the use of one technology for the treatment of both volatile and semivolatile chemicals in the subsurface.

Another example of the use of a treatment train for creosote-contaminated soil and ground water involved (1) product removal using a pumping system, (2) flushing with water and surfactants using pump-and-treat technology, and (3) *in situ* biodegradation of the residual contamination (Kuhn and Piontek, 1989).¹² Each technology was employed in the order of ease of removal of creosote from the subsurface. The treatment train selected was based on a site characterization to identify where the creosote was located and the mass of creosote (including pure product) associated with subsurface phases, i.e., the vadose zone and aquifer materials. The problem assessment identified the following areas of concern: (1) potential off-site migration of pure product; (2) slow leaching of low levels of creosote contaminants sorbed to soil, subsurface, and aquifer materials; and (3) presence of high-molecular-weight polycyclic aromatic compounds that are toxic to human health, are nonvolatile, and have very low water solubilities. Each technology was evaluated in laboratory-scale treatability tests for treatment effectiveness and for ease of application to contaminated materials obtained from the site. Engineering design and implementation was based on results of site characterization, mass balance determinations at the site, and treatability studies.

Information from treatability studies is used to prepare an approach to the engineering design and implementation of a remediation system at a specific site that combines the treatment techniques evaluated to construct an appropriate treatment train. The formulation of a treatment train for a site generally is based upon information from simulations (e.g., mathematical modeling) generated from mass balance studies, treatability studies, and site/soil characterization data.

¹² Kuhn, R.C. and K.R. Piontek. 1989. A Site-Specific In Situ Treatment Process Development Program for a Wood Preserving Site. Paper presented at EPA Technical Program on Oily Waste Fate, Transport, Site Characterization, and Remediation Seminar, Denver, CO, May 17–18.

12.4 MEASUREMENT AND INTERPRETATION OF TREATMENT EFFECTIVENESS

Typically, subsurface samples are taken from a treatability reactor (*in situ* or prepared bed) from laboratory-, bench-, or pilot-scale studies, or from a field site. Waste constituents are extracted from the samples with a solvent or are thermally desorbed. Compound concentration is usually measured in the solvent extract or the thermal desorption stream using chemical instrumentation (e.g., gas or liquid chromatographs with appropriate detectors). This information is termed the *apparent loss* of the compound and refers to the observation that the compound only has disappeared from the solvent or extraction phase, but does not necessarily represent a chemical mass balance (Park et al., 1990 — footnote 3). The change in concentration of the compound in the solvent with time often is used to calculate rate and extent of decrease in concentration of the compound in soil. This information is commonly used to interpret treatment effectiveness for different technologies as well as to determine engineering strategies and management approaches, including (1) time required to attain cleanup target concentrations, and (2) effects of environmental factors or experimental variables (chemical, physical, or biological) on treatment effectiveness.

However, additional information is needed to accurately measure and interpret treatment effectiveness. In order to understand treatment mechanisms and to base the selection of treatment technologies on a rational approach, identification and measurement of distribution among the physical phases that comprise a subsurface system are necessary. In addition, the mechanisms by which a compound may be chemically altered in a subsurface system must be identified and differentiated.

Information obtained about the rate of apparent loss of chemicals from a subsurface extract can be enhanced with information about the (1) interphase transfer potential between solid and gas phases of the subsurface, and (2) mechanisms of interactions of compounds with subsurface phases. This information then provides the basis for a more rational approach to subsurface remediation. Evaluation of remediation technology effectiveness also can be based upon specific media (solid, air) and upon specific mechanisms, such as recovery of the air phase or enhancement of abiotic destruction or biological degradation, to improve treatment. Evaluation of interphase transfer also allows characterization of routes by which chemicals may migrate from the subsurface to the multimedia environment that then may lead to human exposure. Thus, measuring treatment effectiveness based upon interphase transfer potential (a mass balance approach) is also valuable for determining risk reduction and implementing risk management strategies (Park et al., 1990 — footnote 3). The laboratory flask apparatus used for mass balance determinations (Figure 12.4) also can be used to measure and compare potential effectiveness for different treatment scenarios.

12.5 GUIDE TO MAJOR REFERENCES

Table 12.7 provides an index of major references that address general aspects of soil and ground-water remediation in the following categories: (1) health and safety, (2) environmental engineering, (3) general references on soil and ground-water remediation, including bioremediation, (4) treatment of hazardous wastes, (5) remedial action at contaminated sites, (6) vapor phase contaminants, (7) underground storage tank and spill remediation, (8) other contaminants (inorganic, radioactive, and wood preserving sites), (9) treatability studies, and (10) conferences and symposia. Many of the conference series listed in Table 5.12 also address remediation of contaminated soil and ground water. Table 13.7 and Table 14.9 provide indices to major references that focus on treatment and remediation of soil and ground water, respectively.

A major source of information on new developments in technologies for remediating contaminated soil and ground water is the Technology Profiles published by U.S. EPA's Superfund

Innovative Technology Evaluation (SITE) program, which summarizes results of three SITE programs: (1) technology demonstration, (2) emerging technologies, and (3) monitoring and measurement technologies. Summary information on specific projects is available from a number of series of publications: (1) Emerging Technology Summaries and Bulletins, (2) Technology Demonstration Summaries and Bulletins, (3) Treatability Study Bulletins, and (4) Site Technology Capsules. A Technology Evaluation and an Applications Analysis report is published for each completed project in the SITE program. The 10th edition of the SITE Technology Profiles (U.S. EPA, 1999/T12.7) includes a list of available publications from the SITE program, which are available at no cost from CERl as long as they are available, at which time they become available from NTIS (see Preface for information on how to obtain documents from CERl and NTIS).

Other useful information sources from the U.S. EPA include (1) *Bioremediation in the Field*, a periodic newsletter that summarizes information on bioremediation projects (available from CERl); (2) *VISITT* (Vendor Information System for Innovative Treatment Technologies), available on diskette from U.S. EPA/NCEPI (P.O. Box 42419, Cincinnati, OH 45242-0419), which is supported by an intermittent newsletter by the same name; (3) the RREL Treatability Database (Version 5.0 available from Glenn Shaul NNRNL–Cincinnati, 513-569-7408); and (4) periodic Engineering Bulletins and Superfund Engineering Issue Papers, prepared by the Risk Reduction Engineering Laboratory (now called the National Risk Management Research Laboratory) in Cincinnati (U.S. EPA, 1991–1992/T12.7). The Engineering Bulletins and Engineering Issue Papers are typically 7 to 10 pages and available from NCEPI.

From 1992 to 2002 the U.S. EPA Technology Innovation Office published two newsletters, *Ground Water Currents*, which provided information on innovative ground water treatment technologies, and *Tech Trends*, which focused on innovative soil remediation technologies. In 2002 these newsletters were combined into a single newsletter, *Technology News and Trends*. Back issues and subscription information are available on the Internet at <www.clu-in.org> or <www.epa.gov/tio>. CLU-IN is an EPA website that provides hazardous waste cleanup information. EPA's Remediation and Characterization Innovative Technology database (REACHIT: <www.epar-eachit.org>) and the Federal Remediation Technology Roundtable (FRTR: <www.frtr.gov>) are other good sources of information.

Table 12.7 Index to Major References on Soil and Ground Water Remediation Planning

Topic	References
Health and Safety	<u>General</u> : Baldwin (1992), Della-Guistina (1999), Koren and Bisesi (2002), Reese (1999), Vincoli (1999); <u>Field</u> : Andrews (1990), Hislop (1999), National Safety Council (1985), NIOSH/OSHA/USCG/EPA (1985), Streng et al. (1982); <u>Exposure Monitoring/Limits</u> : ACGIH (1992), Ness (1991); <u>Protective Clothing</u> : Forsberg and Mansdorf (1989), Martin and Levine (1993), Schwowe et al. (1985); <u>Radiation</u> : Hallenbeck (1994)
Environmental Engineering	Bailey and Ollis (1986), Corbitt (1990); see also references on general design for source controls in Table 14.9
Soil and Ground Water	Barkley (1993), Boulding (1996), Ehrenfeld and Bass (1983, 1984), Huang and Iskander (1999), Jacobs et al. (2000 — MTBE), Kuo (1998), Liu and Liptak (1999a), Madden and Johnson (1992), Nyer (1993), Russell et al. (1992), Southersan (2001), U.S. EPA (1980, 1991–1992, 1999d, 2001a — costs, 2001c — case studies); <u>Soil</u> : See Table 13.9; <u>Ground Water</u> : See Table 14.9; <u>Bioremediation</u> : Alexander (1994), Flathman and Jerger (1993), Hinchee et al. (1994a, 1994b, 1994c), Irvine and Skidar (1997a, 1997b, 1998), King et al. (1997), Means and Hinchee (1994), Norris et al. (1993a, 1993b), NRC (1993), Skipper and Turco (1995), Thomas et al. (1987), U.S. EPA (1992c, 1993), WEF (1994b), Wilson et al. (1989); <u>In Situ</u> : Gere and Wing (1994), Nyer (2000), U.S. EPA (1995d — hydraulic/pneumatic fracturing); <u>Phytoremediation</u> : Kruger et al. (1997), Terry and Banuelos (1999), U.S. EPA (1999a); <u>NAPLs</u> : Lowe et al. (1999), U.S. EPA (1994a — DNAPLs, 1994b — solvents, 1995b — surfactants, 1995c — cosolvents, 1999b — multiphase extraction), Ward (2000); <u>Thermal Enhancements</u> : Davis (1997, 1998), U.S. EPA (1995a, 2001b); <u>Cleanup Standards</u> : Buonicore (1996), Oliver et al. (1993), WEF (1994a)
Industrial and Hazardous Waste Management/Treatment	Blackman (2001), Celenza (1999a, 1999b, 2000), Cherimissinoff and Graffia (1995 — safety), DeRenzo (1978), Environmental Resource Center Staff (1992), Freeman (1988), Grasso (1993), Grossell and Cowl (1994), HMCRI (various dates), Liu and Liptak (1999b), Madden and Johnson (1992), Martin and Johnson (1987), Moore (2000), O'Brien & Gere Engineering (1988), Oh (2001), Rich and Cherry (1987), Testa (1993), U.S. EPA (1987c, 1989c), Wentsel et al. (1981), WPCF/WEF (1990); <u>Biotreatment</u> : AWWA/EPA (1989), Levin and Gealt (1993), Lewandowski et al. (1989), Omenn (1988), Slonim et al. (1985); <u>Drum/Materials Handling</u> : PEI Associates (1993), Wagner et al. (1986b); <u>Land Treatment</u> : Brown et al. (1983), Loehr et al. (1985), U.S. EPA (1986a); <u>Chemical Spills</u> : Andrews (1992), Hosty and Foster (1992), Pilie et al. (1975), Yang and Bye (1979); <u>Case Studies</u> : Allen et al. (1987)
Remedial Action/Remediation	A.D. Little (1983), ASCE (1999), Barkley (1993), Bartenfelder et al. (1992), Boulding (1996), Brusseau (1999), DOD/ETTC (1994 — screening matrix), Ehrenfeld and Bass (1983, 1984), Meyers (1998), Southersan (1996), U.S. EPA (1985a, 1985b, 1987a — data requirements, 1987b — USTs, 1988 — interim measures guidance, 1989a), Wagner et al. (1986a), Ward et al. (1999); <u>Contracting</u> : Erickson (1992); <u>Construction Quality Management</u> : Richardson (1992), U.S. EPA (1986b); <u>Costs</u> : Lippitt et al. (1986), Yang et al. (1988 — costs); <u>Source Controls</u> : See Table 14.9; <u>State Guidance Documents</u> : California Department of Health Services (1986), California LUFT Task Force (1988), Dixon (1992), Simmons (1989); <u>Case Studies</u> : Cockerin and Furmin (1988), Kingsbury and May (1986), Neely et al. (1981), U.S. EPA (1984, 1989g); <u>Alternative/Innovative Technologies</u> : Murdoch et al. (1988), U.S. EPA (1991a, 1992d, 1999c), Young et al. (1990)
Vapor Phase	<u>Landfill Gases/Methane</u> : Campbell et al. (1991), Geyer (1972), Ghassemi et al. (1985), Horz (1986), Pohland and Harper (1986); <u>Hazardous Waste Volatilization</u> : Dupont and Reineman (1986)
Hydrocarbon/Petroleum/UST/Spill Remediation	API (1980, 1982), Calabrese and Kostecki (1992), California LUFT Task Force (1988), Cole (1994), Dixon (1992), Downey et al. (1999), FDER (1992), Heard et al. (1986), Hinchee et al. (1994c), Kostecki and Calabrese (1991), Noonan and Curtis (1989/T14.9), Preslo et al. (1988), Simmons (1989), Thomas et al. (1987), U.S. EPA (1987b, 1990a), Wilson et al. (1989)
Other Contaminants	<u>Inorganics</u> : Means and Hinchee (1994 — metals), SAI Corp (1992 — arsenic and mercury), SenGupta (2002); <u>PCBs</u> : U.S. EPA (1990b); <u>Radioactive</u> : See Table 13.9; <u>Wood Preserving Sites</u> : Barth et al. (1990), Sudell et al. (1992)

Table 12.7 Index to Major References on Soil and Ground Water Remediation Planning (Continued)

Topic	References
Treatability Studies	U.S. EPA (1986a, 1989b, 1991b, 1992a, 1992b); <u>Batch Tests</u> : Roy et al. (1992)
Conferences/Symposia	<u>Series</u> : HMCRI Bioremediation Series (1988–1989), HMCRI FER Series (1992–1994), HMCRI RCRA Series (1984–1990), HMCRI Superfund Series (1980–1997), NWWA/API (1984–2002), NWWA/NGWA Aquifer-NOAC Series (1981–1997), U.S. EPA Waste Disposal Symposium Series (1975–1993); <u>University of Massachusetts Petroleum/Hydrocarbon Contaminated Soil Series</u> : Calabrese and Kostecki (1989 — 3rd, 1991 — 5th), Kostecki and Calabrese (1989 — 2nd, 1990 — 4th); <u>West Coast Hydrocarbon Contaminated Soils and Groundwater Series</u> : Calabrese and Kostecki (1992 — 2nd), Kostecki and Calabrese (1991 — 1st); <u>Other Conferences</u> : AWWA/EPA (1990 — contaminated soils), Kostecki and Calabrese (1992 — diesel fuel contaminated soil), National Center for Ground Water Research (1992), McCarthy and Wobber (1993), Schmidt (1985), TNO/BMFT (1985, 1989 — contaminated soils)

Battelle Remediation Conference/Symposium Proceedings Series

International Conference on Remediation of Contaminated Sediment

[First], Venice, Italy, October 2001, 3 vols. published in 2002, various editors

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| Vol. S1-1 | Characterization of Contaminated Sediments, 330 pp. |
| Vol. S1-2 | Management of Contaminated Sediments, 285 pp. |
| Vol. S1-3 | Remediation and Beneficial Reuse of Contaminated Sediments, 465 pp. |

Second, Monterey, CA, May 2002

International In Situ and On-Site Bioremediation Symposium (Biennial)

[First], San Diego, April 1991

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|-----------|--|
| Vol. 1(1) | On-Site Bioreclamation: Processes for Xenobiotic and Hydrocarbon Treatment |
| Vol. 1(2) | <i>In Situ</i> Bioreclamation: Applications and Investigations for Hydrocarbon and Contaminated Site Remediation |

Second, San Diego, April 1993, 5 vols. published in 1994 by CRC Press, various editors

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|-----------|---|
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| Vol. 2(2) | Hydrocarbon Bioremediation |
| Vol. 2(3) | Applied Biotechnology for Site Remediation |
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| Vol. 2(5) | Air Sparging for Site Bioremediation |

Third, San Diego, April 1995, 11 vols. published in 1995, various editors

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|------------|---|
| Vol. 3(1) | Intrinsic Bioremediation, 278 pp. |
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| Vol. 3(3) | Bioaugmentation for Site Remediation, 276 pp. |
| Vol. 3(4) | Bioremediation of Chlorinated Solvents, 350 pp. |
| Vol. 3(5) | Monitoring and Verification of Bioremediation, 286 pp. |
| Vol. 3(6) | Applied Bioremediation of Petroleum Hydrocarbons, 550 pp. |
| Vol. 3(7) | Bioremediation of Recalcitrant Organics, 380 pp. |
| Vol. 3(8) | Microbial Processes for Bioremediation, 374 pp. |
| Vol. 3(9) | Biological Unit Processes for Hazardous Waste Treatment, 370 pp. |
| Vol. 3(10) | Bioremediation of Inorganics, 184 pp. |
| | Bioremediation Series Cumulative Indices: 1991–1995, 180 pp. |

Table 12.7 Index to Major References on Soil and Ground Water Remediation Planning (Continued)

Topic	References
<i>Fourth, New Orleans, April 1997, 5 vols. published in 1997, B.C. Alleman and A. Leeson (eds.)</i>	
Vol. 4(1)	<i>In Situ</i> and On-Site Bioremediation, 590 pp. [Natural attenuation and biodegradation of petroleum hydrocarbons]
Vol. 4(2)	<i>In Situ</i> and On-Site Bioremediation, 686 pp. [Bioremediation of media contaminated by PAHs, PCBs and chlorinated aromatics, explosives and nitroaromatics, pesticides and herbicides]
Vol. 4(3)	<i>In Situ</i> and On-Site Bioremediation, 570 pp. [Treatment of soil and ground water contaminated with chlorinated solvents, manufactured gas plants residuals, and inorganics]
Vol. 4(4)	<i>In Situ</i> and On-Site Bioremediation, 658 pp. [Use of microbial, physical, and chemical processes to support and enhance <i>in situ</i> bioremediation]
Vol. 4(5)	<i>In Situ</i> and On-Site Bioremediation, 752 pp. [Advanced technologies for promoting and monitoring bioremediation, including wastewater, landfill leachates, and low-permeability soils]
<i>Fifth, 1999, 8 vols. published in 1999, B.C. Alleman and A. Leeson (eds.)</i>	
Vol. 5(1)	Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons and Other Organic Compounds, 402 pp.
Vol. 5(2)	Engineered Approaches for <i>In Situ</i> Bioremediation of Chlorinated Solvent Contamination, 336 pp.
Vol. 5(3)	<i>In-Situ</i> Bioremediation of Petroleum Hydrocarbon and Other Organic Compounds, 588 pp.
Vol. 5(4)	Bioremediation of Metals and Inorganic Compounds, 190 pp.
Vol. 5(5)	Bioreactor and <i>Ex Situ</i> Biological Treatment Technologies, 256 pp.
Vol. 5(6)	Phytoremediation and Innovative Strategies for Specialized Remedial Applications, 340 pp.
Vol. 5(7)	Bioremediation of Nitroaromatic and Haloaromatic Compounds, 302 pp.
Vol. 5(8)	Bioremediation Technologies for Polycyclic Aromatic Hydrocarbon Compounds, 358 pp.
<i>Sixth, San Diego, June 2001, 10 vols. published in 2001, various editors</i>	
Vol. 6(1)	Bioremediation of MTBE, Alcohols, and Ethers, 264 pp.
Vol. 6(2)	Natural Attenuation of Environmental Contaminants, 320 pp.
Vol. 6(3)	Bioremediation of Energetics, Phenolics, and Polycyclic Aromatic Compounds, 324 pp.
Vol. 6(4)	Innovative Methods in Support of Bioremediation, 205 pp.
Vol. 6(5)	Phytoremediation, Wetlands and Sediment, 392 pp.
Vol. 6(6)	<i>Ex Situ</i> Biological Treatment Technologies, 432 pp.
Vol. 6(7)	Anaerobic Degradation of Chlorinated Solvents, 394 pp.
Vol. 6(8)	Bioaugmentation, Biobarriers, and Biogeochemistry, 264 pp.
Vol. 6(9)	Bioremediation of Inorganic Compounds, 383 pp.
Vol. 6(10)	<i>In Situ</i> Aeration and Aerobic Remediation, 360 pp.
<i>Seventh, Orlando, FL, June 2003 [publication pending]</i>	
<i>International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Biennial)</i>	
<i>First, Monterey, CA, 1998, 6 vols. published in 1998, G.B. Wickramanayake and R.E. Hinchee (eds.)</i>	
Vol. C1-1	Risk, Resource, and Regulatory Issues: Remediation of Chlorinated and Recalcitrant Compounds, 336 pp.
Vol. C1-2	Nonaqueous Phase Liquids: Remediation of Chlorinated and Recalcitrant Compounds, 256 pp.
Vol. C1-3	Natural Attenuation: Chlorinated and Recalcitrant Compounds, 392 pp.
Vol. C1-4	Bioremediation and Phytoremediation: Chlorinated and Recalcitrant Compounds, 316 pp.
Vol. C1-5	Physical, Chemical, and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds, 486 pp.

Table 12.7 Index to Major References on Soil and Ground Water Remediation Planning (Continued)

Topic	References
Vol. C1-6	Designing and Applying Treatment Technologies: Remediation of Chlorinated and Recalcitrant Compounds, 366 pp.
<i>Second, Monterey, CA, May 2000, 7 vols. published in 2000, various editors</i>	
Vol. C2-1	Risk, Regulatory, and Monitoring Issues: Remediation of Chlorinated and Recalcitrant Compounds, 406 pp.
Vol. C2-2	Treating Dense Nonaqueous-Phase Liquids (DNAPLs): Remediation of Chlorinated and Recalcitrant Compounds, 252 pp.
Vol. C2-3	Natural Attenuation Considerations and Case Studies: Remediation of Chlorinated and Recalcitrant Compounds, 242 pp.
Vol. C2-4	Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds, 524 pp.
Vol. C2-5	Physical and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds, 332 pp.
Vol. C2-6	Chemical Oxidation and Reactive Barriers: Remediation of Chlorinated and Recalcitrant Compounds, 450 pp.
Vol. C2-7	Case Studies in the Remediation of Chlorinated and Recalcitrant Compounds, 406 pp.
<i>Third, Monterey, CA, May 2002</i>	

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* See Preface for information on how to obtain documents from CERL and NTIS.

**In 1992 the National Water Well Association (NWWA) changed its name to the National Ground Water Association (NGWA).

Remediation of Contaminated Soils

13.1 GENERAL APPROACHES TO SOIL REMEDIATION

Soil remediation techniques are applied to the vadose zone ranging from the soil rooting zone to the capillary fringe (Section 2.4.2), and to situations where the saturated zone is engineered to become unsaturated (e.g., when ground water is pumped to create an unsaturated zone). Table 12.5 provides information on the suitability of different treatment technologies for contaminated soils and sludges. Remediation techniques for contaminated soils can be broadly classified as follows: (1) physical and chemical treatment, (2) biological treatment, (3) fixation or encapsulation), and (4) thermal destruction. Table 13.1 through Table 13.4 provide the following additional summary information on specific techniques in these five categories:

- Ways in which technique can be used (*in situ*, prepared bed, or in-tank — discussed in this section)
- The function of the treatment method (detoxification, separation, volume reduction, immobilization)
- Types of wastes that are amenable to treatment using the technique
- Possible residuals or transformation products
- Possible limitations to the technique

In situ treatment consists of treating contaminated soil in place; i.e., the contaminated soil is not moved from the ground. This chapter focuses on *in situ* treatment methods, with special emphasis on soil vacuum extraction (Section 13.2) and bioremediation (Section 13.3).

In a *prepared bed* system, the contaminated soil may be either (1) physically moved from its original site to a newly prepared area, which has been designed to enhance treatment and prevent transport of contaminants from the site; or (2) removed from the site to a storage area while the original location is prepared for use, and then returned to the bed, where treatment is accomplished. Preparation of the bed may include placement of a clay or plastic liner to retard transport of contaminants from the site or addition of uncontaminated soil to provide an additional treatment medium. Treatment may be enhanced with biological and physical/chemical methods, as with *in situ* systems. Prepared bed treatment approaches are based on modifications of principles developed in the areas of land application of solid and liquid wastes and in land treatment of hazardous wastes. Section 13.5 discusses prepared bed systems in more detail.

In-tank treatment involves removing the contaminated soil and treating it in a vessel or other system designed to optimize treatment efficiency. Many specific treatment techniques can be used *in situ*, as prepared beds, or in-tank, while others are limited to a specific treatment category. For example, *soil flushing* and *soil washing* (Table 13.1) involve the same principles, but the former is

Table 13.1 Summary of Physical and Chemical Treatment Methods for Contaminated Soil

Method	Characteristics	Limitations
Soil vacuum extraction (SVE)	Treatment Category: <i>In situ</i> ; prepared bed Function: Separation Amenable Wastes: Volatile organics and toxic metals; may be enhanced by the use of steam Possible Residuals/Transformation Products: Volatile organics and volatile toxic metals	Soil heterogeneity (e.g., permeability, texture — see Figure 13.4 for most unfavorable textures); not applicable to saturated materials or miscible compounds
Soil washing	Treatment Category: In-tank Function: Separation; volume reduction Amenable Wastes: Organics and inorganics; most suitable for soils contaminated by only a few specific chemicals Possible Residuals/Transformation Products: Extracted materials; water/flushing agent mix	Unfavorable contaminant separation coefficients; less effective with complex mixtures of waste types and variation in waste composition Unfavorable Soil Characteristics: High humic content, soil/solvent reactions, high silt and clay content, and clay soils containing semivolatiles Unfavorable washing fluid characteristics: Difficult recovery of solvent or surfactant, poor treatability of washing fluid, reduction of soil permeability, and high toxicity of washing fluid
Soil flushing	Treatment Category: <i>In situ</i> Function: Separation; volume reduction Amenable Wastes: Organics and inorganics; most suitable for soils contaminated by only a few specific chemicals Possible Residuals/Transformation Products: Extracted materials; water/flushing agent mix	Similar to soil flushing above; additional unfavorable soil characteristics include high soil variability; requires containment of leachate and ground water to prevent off-site ground-water contamination
Low-temperature thermal stripping (including radio frequency heating)	Treatment Category: <i>In situ</i> ; in-tank Function: Separation Amenable Wastes: Compounds of low water solubility and high volatility Possible Residuals/Transformation Products: Off gas; spent carbon or ash from afterburner; processed soil; hazardous emissions from <i>in situ</i> applications	Limited to organics with Henry's law constant greater than 3.0×10^{-3} atm-m ⁻³ /mol and boiling points less than 800°; more effective for soils with low contents of organic matter and moisture
Glycolate dechlorination	Treatment Category: <i>In situ</i> ; in-tank Function: Detoxification Amenable Wastes: Dehalogenation of aromatic halide compounds Possible Residuals/Transformation Products: Water–reagent mix; reaction products	Heat and excess reagent required for soils with greater than 20% moisture, contaminant concentrations greater than 5%, and soils containing competing reactive metals such as aluminum
Neutralization	Treatment Category: <i>In situ</i> ; prepared bed; in-tank Function: Detoxification; immobilization Amenable Wastes: Waste acids and alkalis to reduce reactivity and corrosiveness Possible Residuals/Transformation Products: Precipitated salts	Compatibility of waste and treatment chemical to prevent formation of more toxic or hazardous compounds
Oxidation	Treatment Category: <i>In situ</i> ; prepared bed; in-tank Function: Detoxification Amenable Wastes: Cyanides and oxidizable compounds Possible Residuals/Transformation Products: Oxidized reaction products	Possible explosive reactions; production of more toxic or hazardous products; nonselective
Photolysis	Treatment Category: Prepared bed Function: Detoxification Amenable Wastes: Dioxins, nitrated wastes	Inability of light to penetrate the soil

Table 13.1 Summary of Physical and Chemical Treatment Methods for Contaminated Soil (Continued)

Method	Characteristics	Limitations
Photolysis (continued)	Possible Residuals/Transformation Products: Reaction products	
Precipitation	Treatment Category: <i>In situ</i> ; prepared bed; in-tank Function: Separation; volume reduction; immobilization Amenable Wastes: Metals; certain anions Possible Residuals/Transformation Products: Precipitated metals	Unfavorable effects on soil permeability; long-term stability unknown
Reduction	Treatment Category: <i>In situ</i> ; prepared bed; in-tank Function: Detoxification Amenable Wastes: Chromium, silver, and mercury Possible Residuals/Transformation Products: Reduced reaction products	Possible explosive reactions; production of more toxic or hazardous products; nonselective
Carbon adsorption	Treatment Category: <i>In situ</i> ; prepared bed Function: Separation; immobilization Amenable Wastes: Organic wastes with high molecular weight and boiling points and low solubility and polarity Possible Residuals/Transformation Products: Processed soil	Long-term stability unknown
Ion exchange	Treatment Category: <i>In situ</i> ; prepared bed Function: Separation; immobilization Amenable Wastes: Metal contaminants Possible Residuals/Transformation Products: Processed soil	Selectivity/competition limitations; pH requirements

Source: Adapted from Sims and Sims (1991b).

used for *in situ* treatment, whereas the latter applies to in-tank treatment. All of the thermal treatment methods in Table 13.4 are classified as in-tank methods.

13.2 SOIL VACUUM EXTRACTION

Soil vacuum extraction (SVE), also referred to as *forced air venting* and *in situ air stripping*, involves extraction of air and contaminants from unsaturated soil. In contrast to a static equilibrium soil system where evaporation of a chemical is equal to the condensation of the chemical, with SVE, clean air is injected or passively flows into the unsaturated zone. Volatile chemicals then partition from soil water into soil air, with relative partitioning based on the air–water partition coefficient (K_h) or Henry’s law constant, and the vapor-laden air is removed using vacuum extraction wells.

Typically, components of an SVE system consist of vacuum extraction wells, air inlet wells, and vapor monitoring wells distributed across a contaminated site, and a blower(s) to control airflow (Figure 13.1). Extraction wells may be placed vertically or horizontally, although vertical alignment is typical for deeper contamination zones and for residues in radial flow patterns (Hutzler et al., 1990).¹ Schematics of a gas extraction well and a gas monitoring well are presented in Figure 13.2a and b, respectively.

13.2.1 Significant Chemical Properties

Important system variables that may affect the performance of an SVE include properties of the chemical, such as vapor pressure and volatilization, and properties of the site, such as soil

¹Hutzler, N.J., B.E. Murphy, and J.S. Gierke. 1990. State of Technology Review: Soil Vapor Extraction Systems. EPA/600/2-89/024 (NTIS PB89-195184).

Table 13.2 Summary of Biological Treatment Methods for Contaminated Soil

Method	Characteristics	Limitations
Aerobic bioremediation	Treatment Category: <i>In situ</i> ; prepared bed; in-tank Function: Detoxification Amenable Wastes: Biodegradable organic wastes (see Table 3.11) Possible Residuals/Transformation Products: Hazardous volatile emissions; incomplete and possibly hazardous degradation products; leachates in soil systems	Ability to control environmental factors conducive to biodegradation; formation of more toxic or hazardous transformation products Prepared Bed: Areal limitation due to cost of bed preparation
Anaerobic bioremediation	Treatment Category: <i>In situ</i> ; prepared bed; in-tank Function: Detoxification Amenable Wastes: Certain halogenated organics (Table 3.11) Possible Residuals/Transformation Products: Similar to aerobic, plus carbon dioxide, methane, and other gases	May require long treatment periods; incomplete treatment, possibly requiring aerobic conditions to complete degradation process
Biological seeding	Treatment Category: <i>In situ</i> ; prepared bed; in-tank Function: Detoxification Amenable Wastes: Many biodegradable organic wastes Possible Residuals/Transformation Products: Similar to aerobic bioremediation	Survival and activity of organisms in introduced environment (affected by environmental factors and competition with native species)
Composting	Treatment Category: Prepared bed; in-tank Function: Detoxification Amenable Wastes: Biodegradable organic wastes Possible Residuals/Transformation Products: Similar to aerobic bioremediation, plus runoff water	Maintenance of optimum environmental conditions for biological activity; requires large amounts of compost materials mixed with only about 10% wastes
Enzyme addition	Treatment Category: <i>In situ</i> ; prepared bed; in-tank Function: Detoxification Amenable Wastes: Certain biodegradable organic wastes Possible Residuals/Transformation Products: Similar to aerobic bioremediation	Activity and stability of introduced enzymes in natural systems

Source: Adapted from Sims and Sims (1991b).

moisture content, soil texture, and distribution of contaminants. Vapor pressure is important when a chemical occurs in a pure phase in the subsurface. Vapor pressures above 14 mmHg at 20°C are desirable for application of SVE. Vapor pressure values for selected subsurface contaminants are given in [Table 13.5](#). When chemicals are distributed in the water phase in the soil, the Henry's law constant is important, and a dimensionless Henry's constant above 0.01 is desirable for use of SVE.

13.2.2 Significant Soil Properties

Since movement of volatile organic compounds (VOCs) is generally 10,000 times faster in a gas phase than in a water phase, VOC removal is expected to be enhanced by decreasing soil moisture. However, when soil is very dry, which may occur when dry air is drawn through soil, VOCs may adsorb directly onto mineral surfaces, where the magnitude of sorption is increased and, consequently, volatilization is decreased. Henry's law constant is not appropriate under these conditions, since partitioning is between air and soil phases only. When moisture is added to soil, the effect is reversible. The moisture content at which a decrease in vapor density becomes apparent is often termed the *critical moisture content* and generally is equivalent to approximately a mono-

Table 13.3 Summary of Fixation/Encapsulation Methods for Contaminated Soil

Method	Characteristics	Limitations
Cement solidification	Treatment Category: In-tank; <i>in situ</i> Function: Storage; immobilization Amenable Wastes: Metal cations, latex, and solid plastic wastes Possible Residuals/Transformation Products: Leachates; hazardous volatile emissions; solidified waste materials	Incompatible with large amounts of dissolved sulfate salts or metallic anions such as arsenates or borates; setting time increased by presence of organic matter, lignite, silt, or clay; requires complete and uniform mixing of soils and reagents; long-term stability unknown
Glassification/vitrification	Treatment Category: In-tank; <i>in situ</i> Function: Storage; immobilization Amenable Wastes: Inorganics and some organics in liquids and contaminated soils Possible Residuals/Transformation Products: Leachates; hazardous volatile emissions; glassified or vitrified waste materials; aqueous scrub solution	Long-term stability unknown; high energy requirements, especially with high soil water contents and low permeability; electrical shorting caused by buried metal drums; possible underground fire from combustible materials; volatile metals near surface may enter air; site may require runoff controls
Lime solidification (silicate)	Treatment Category: In-tank; <i>in situ</i> Function: Storage; immobilization Amenable Wastes: Metals, waste oils, and solvents Possible Residuals/Transformation Products: Leachates; hazardous volatile emissions; solidified waste materials	Long-term stability unknown; incompatible with borates, sulfates, carbohydrates; requires complete and uniform mixing of soils and reagents
Thermoplastic microencapsulation	Treatment Category: In-tank; <i>in situ</i> Function: Volume reduction; storage; immobilization Amenable Wastes: Complex, difficult to treat hazardous wastes Possible Residuals/Transformation Products: Leachates; hazardous volatile emissions; encapsulated waste materials	Not suitable for wastes with high water content; strongly oxidizing contaminants, anhydrous inorganic salts, tetraborates, iron and aluminum salts, and organics with low molecular weights and high vapor pressures; long-term stability unknown; requires complete and uniform mixing of soils and reagents

Source: Adapted from Sims and Sims (1991b).

layer of water molecules coating the soil particles (Spencer et al., 1969, 1973).² Johnson and Sterrett (1988)³ noted that dichloropropane concentrations were correlated with ambient air moisture during the use of SVE at a site in Benson, AZ.

If contaminated soil contains immiscible fluids in the form of oils, (e.g., petroleum hydrocarbons), the four-compartment system discussed previously is operative (water, air, oil, and soil, as discussed in Section 12.1). In this system, chemical volatility will be affected by the chemical vapor pressure and mole fraction within the immiscible oil fluid, and governed by Raoult's law:

$$P_a = X_a P_a^o \quad (13.1)$$

where:

P_a = vapor pressure of solvent over solution (mmHg)

X_a = mole fraction of solvent in solution

P_a^o = vapor pressure of pure solvent (mmHg)

For contamination by hydrocarbons with multiple components, volatilization will proceed such that lower-molecular-weight chemicals will volatilize before higher-molecular-weight compounds.

² Spencer, W.F., M.M. Cliath, and W.J. Farmer. 1969. Vapor Density of Soil-Applied Dieldrin as Related to Soil-Water Content, Temperature and Dieldrin Concentration. Soil Sci. Soc. Am. Proc. 33:509–511. Spencer, W.F., W.J. Farmer, and M.M. Cliath. 1973. Pesticide Volatilization. Residue Reviews 49:1–47.

³ Johnson, J.J. and R.J. Sterrett. 1988. Analysis of In Situ Air Stripping Data. In: Proc. 5th National Conference on Hazardous Waste and Hazardous Materials, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 451–455.

Table 13.4 Summary of Thermal Treatment Methods for Contaminated Soil

Method	Characteristics	Limitations
Fluidized bed	Treatment Category: In-tank Function: Volume reduction; detoxification Amenable Wastes: Halogenated and nonhalogenated organics; inorganic cyanides Possible Residuals/Transformation Products: Off gases (possibly acidic and with incomplete combustion products); treated materials with residual metals; fly ash; scrubber water	High maintenance requirements; waste size and homogeneity requirements; applicable to wastes with low sodium and metal contents
Rotary kiln	Treatment Category: In-tank Function: Volume reduction; detoxification Amenable Wastes: Halogenated and nonhalogenated organics; inorganic cyanides Possible Residuals/Transformation Products: Similar to fluidized bed	High particulate emissions; requires small particle size, so may require size reduction equipment
Infrared	Treatment Category: In-tank Function: Volume reduction; detoxification Amenable Wastes: Halogenated and nonhalogenated organics; inorganic cyanides Possible Residuals/Transformation Products: Similar to fluidized bed	Requires small particle size, so may require size reduction equipment
Pyrolysis	Treatment Category: In-tank Function: Volume reduction; detoxification Amenable Wastes: Wastes not conducive to conventional incineration; waste with volatile metals or recoverable residues Possible Residuals/Transformation Products: Nonvolatile char and ash (metals, salts, and particulates)	Small capacity

Source: Adapted from Sims and Sims (1991b).

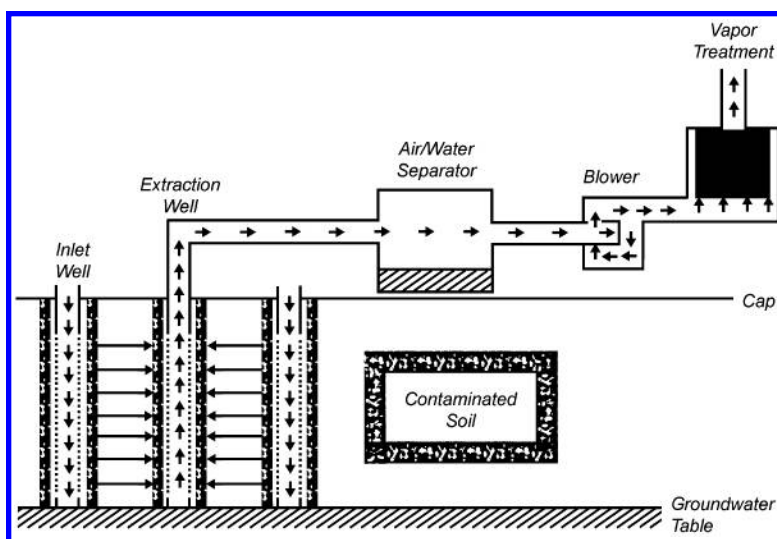


Figure 13.1 Typical components of a soil vacuum extraction system (Sims and Sims, 1991b, after Hutzler et al., 1990).

Through this process of weathering of the waste–soil mixture, SVE extraction efficiency is observed to decrease to less than 10% when the fraction of gasoline remaining is approximately 40% (Figure 13.3). Therefore, measuring general parameters such as total hydrocarbons is not sufficient to indicate the removal efficiency of individual constituents.

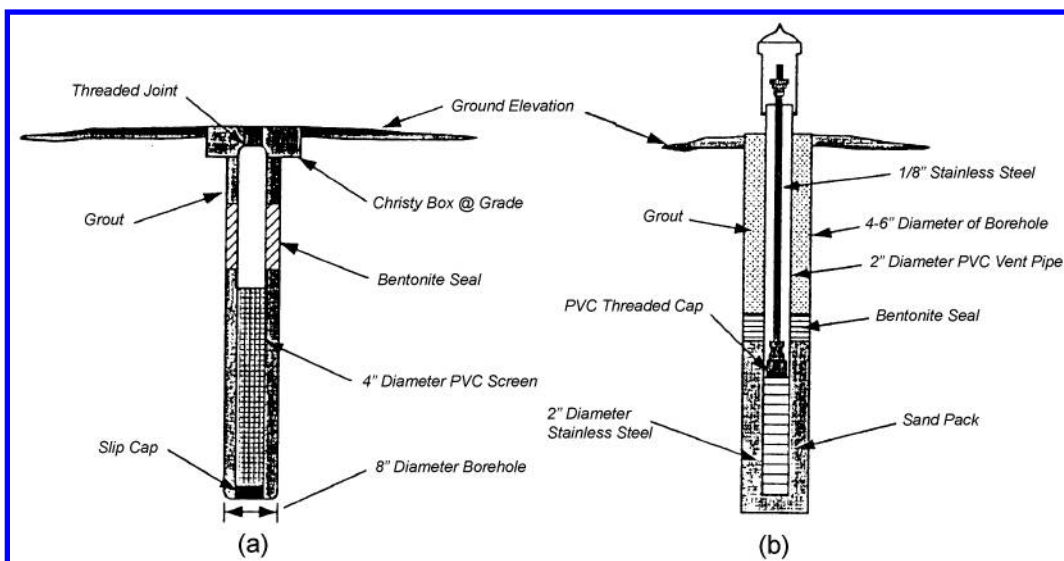


Figure 13.2 Soil vacuum extraction system: (a) gas extraction well; (b) gas monitoring well (Sims and Sims, 1991b).

Table 13.5 Comparative Vapor Pressures and Henry's Constants

Compound	Vapor Pressure (mmHg)	Henry's Constant (dimensionless)
Methylene chloride	362	0.13
Acetone	200	Miscible
Methyl ethyl ketone (MEK)	100	0.001
1,2-Dichloroethane (EDC)	61	0.037
Bis (chloromethyl) ether	30	0.008
Phenol	0.53	0.00002
Mercury (Hg°)	0.0012	0.48
PCB-1260	4.05×10^{-5}	0.30

Source: Sims and Sims (1991b).

Soil texture strongly influences air permeability and, consequently, serves as a good indicator of suitability of a site for SVE. In less permeable media, such as glacial till and clayey soils, secondary permeability or porosity (fractures) will dominate airflow. There will be rapid removal of VOCs in fractures and slow removal in the soil matrix. In more permeable media, such as sands, sandy loams, and loamy sands, SVE is appropriate (Figure 13.4). Pneumatic pump tests in the field are recommended for site-specific evaluation of SVE application.

Due to release of VOCs from the soil matrix, when extraction wells are temporarily turned off, concentrations of VOC increase in soil air (referred to as VOC rebound effect), with an equilibrium concentration that is determined by Henry's law constant. When blowers are turned on, an increase in the concentration of extracted vapor from the soil will be observed. Diffusive release from subsurface stratigraphy of less permeability will cause the slow continual release of chemicals into the soil gas phase (Figure 13.5).

13.2.3 Design Considerations

Design considerations that affect SVE include extraction well spacing and extraction well depth. As permeability decreases, well spacing decreases; typical well spacings of 10 to 30 m are common (Figure 13.6). Also, air circulation generally is not significant below the screened interval for

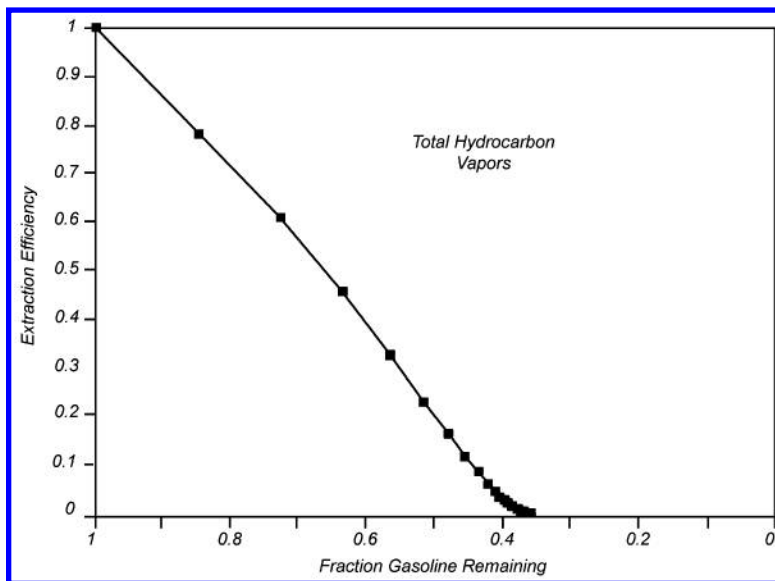


Figure 13.3 Soil vacuum extraction efficiency based on total hydrocarbon vapors (Sims and Sims, 1991b).

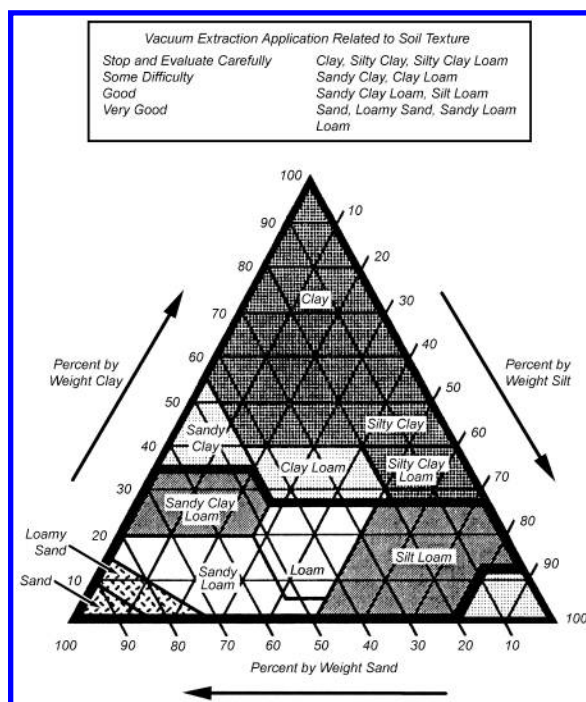


Figure 13.4 Suitability of soil vacuum extraction related to soil texture (Sims and Sims, 1991b).

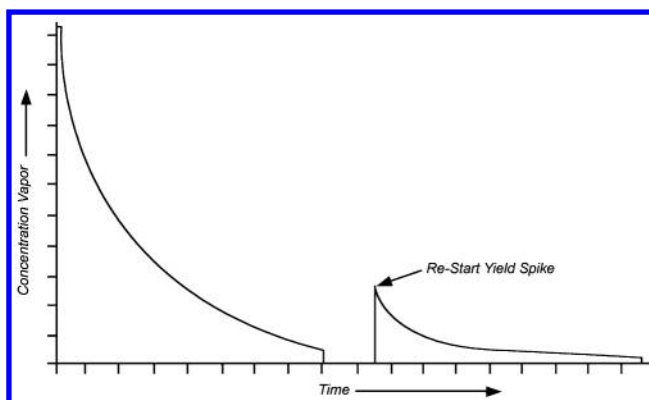


Figure 13.5 Volatile organic compound (VOC) rebound effect with SVE stop and restart (Sims and Sims, 1991b).

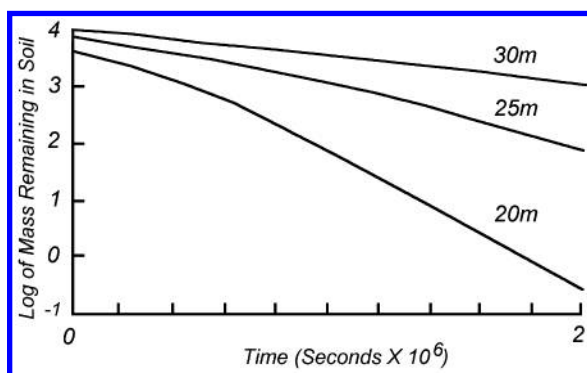


Figure 13.6 Effect of well spacing on total solute mass remaining in soil with vacuum extraction (Sims and Sims, 1991b).

extraction wells. Where contamination is deep and permeability is high throughout the soil profile, the slotted (screened) interval should be extended to the maximum depth possible to maximize treatment, rather than slotted fully vertically. Placement of horizontal extraction wells using directional drilling techniques (described in Table 9.3) in zones with the highest contaminant concentrations can significantly improve vapor recovery.

13.2.4 Enhanced Biodegradation

A promising application of SVE is for enhancement of biodegradation of volatile and semi-volatile chemicals in soils. SVE provides air to the vadose zone, and thus carries oxygen that can be used as the terminal electron acceptor (TEA) by soil microorganisms to biodegrade chemicals. Air has a much greater potential than water for delivering oxygen to soil on a weight-to-weight and volume-to-volume basis. The amount of air required to deliver 1 lb of oxygen is 4 lb. In comparison, 100,000 lb of air-saturated ground water is required to deliver 1 lb of oxygen. Oxygen provided by air is more easily delivered since the fluid is less viscous than water; higher oxygen concentrations in air also provide a large driving force for diffusion of oxygen into less permeable areas within a soil formation.

Hinchee and Downey (1990)⁴ successfully applied SVE to enhance biodegradation of petroleum hydrocarbons in JP-4 jet fuel at Hill Air Force Base, Ogden, UT, by increasing subsurface oxygen

⁴ Hinchee, R. and D. Downey. 1990. In Situ Enhanced Biodegradation of Petroleum Distillates in the Vadose Zone. In: Proceedings of the International Symposium on Hazardous Waste Treatment: Treatment of Contaminated Soils (Cincinnati, OH). Air and Waste Management Association, Pittsburgh, PA.

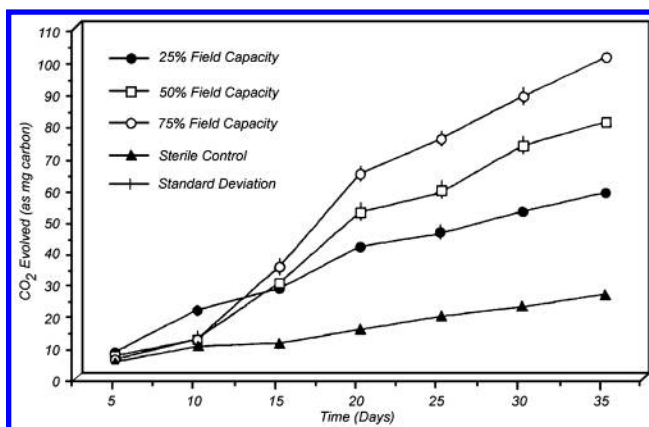


Figure 13.7 Enhanced bioremediation of gasoline-contaminated soil using soil vacuum extraction, nutrient additions and moisture control (Sims and Sims, 1991b).

concentrations. Soil moisture was found to be a sensitive variable affecting biodegradation, with increased soil moisture (from 20 to 75% field capacity) related to increased biodegradation (Figure 13.7). Monitoring carbon dioxide and oxygen concentrations, as well as estimating the mass of VOC biodegraded, is recommended for evaluating potential enhancement of biodegradation using SVE.

13.2.5 Passive Soil Vapor Extraction

Passive soil vapor extraction relies on naturally occurring changes in barometric pressure for contaminant transport in the vadose zone. Fluctuations in barometric pressure can cause changes in the pressure of vadose zone gases, resulting in airflow from areas of high pressure in the subsurface to areas of lower pressure. Rossabi (2000/T13.9) reports on the state of the art of barometric pumping and potential application for remediation of volatile contaminants in the vadose zone.

Fluctuations of barometric pressure are due primarily to diurnal temperature changes or changes in local weather. These pressure fluctuations can be monitored in wells that are completed in the vadose zone and connected to the surface. In addition to the extraction of volatile organic compounds from the subsurface, passive venting wells can also be utilized to bring oxygen to the subsurface to stimulate biodegradation (Zachary, 1993; Zwick, 1994/T13.9). Under the right conditions, both barometric pumping and barometric injection can be used to control the transport and migration of subsurface gasses. Higher flow rates associated with bioventing and traditional SVE are sacrificed in order to achieve either removal or injection at lower costs.

Passive soil vapor extraction can also be used for subsurface characterization such as determining the pneumatic conductivity (Rossabi, 1999/T13.9). Additionally, insight can be gained into the mass and distribution of contaminants by evaluating the expelled vapors during barometric pumping cycles. It is important that wells completed in the vadose zone and extending to the surface be fitted with one-way check valves to more accurately reflect mass transport in the subsurface.

13.3 BIOREMEDIATION

Biotic reactions in the subsurface, including definitions and mechanisms, are addressed in Section 3.5. *In situ* soil remedial measures using biological processes can reduce or eliminate continuing or potential ground-water contamination, thus reducing the need for extensive ground-water monitoring and treatment requirements (Wilson, 1981, 1982, 1983/T9.10). This section focuses on *in situ* bioremediation. Table 13.2 provides some summary information on other bioremediation techniques.

In situ bioremediation involves the use of naturally occurring microorganisms (in contrast to genetically engineered microorganisms) to degrade and detoxify hazardous constituents in the soil at a contaminated site to protect public health and the environment. The use of bioremediation techniques in conjunction with chemical and physical treatment processes, i.e., the use of a treatment train, is an effective means for comprehensive site-specific remediation (Ross et al., 1988).⁵

Components of soil bioremediation systems generally include (1) *delivery systems* (such as injection nozzles, plows, and irrigation systems), supply water, nutrients, oxygen, organic matter, specialized microorganisms, and other amendments as required, and (2) *run-on and runoff controls* for moisture control and waste containment (Chambers et al., 1990/T13.9; Sims et al., 1984/T13.9).

13.3.1 Approaches to *In Situ* Biological Treatment

Four approaches are generally used for *in situ* biological treatment: (1) enhancement of biochemical mechanisms for detoxifying or degrading chemicals, (2) augmentation with exogenous acclimated or specialized microorganisms originating from uncontaminated or contaminated environments, (3) application of cell-free enzymes, and (4) vegetative uptake (Chambers et al., 1990/T13.9). Enhancement of biochemical mechanisms may involve (1) control of soil factors such as contaminant concentrations that do not severely inhibit microbial activity, soil moisture, pH, nutrients, and temperature in order to optimize microbial activity; (2) addition of organic amendments to stimulate cooxidation or cometabolism; (3) control of soil oxygen by moisture control to accomplish aerobic or anaerobic biodegradation; and (4) addition of colloidal gas aphrons (microscopic bubbles of gas) to increase the concentration of terminal electron acceptors (oxygen) in the soil and thereby enhance aerobic biodegradation.

13.3.2 Significant Environmental Parameters

The environmental factors presented in Table 13.6, as well as waste and soil/site characteristics identified in Table 12.1, interact to affect microbial activity at a specific contaminated site. Computer modeling techniques are useful design and evaluation tools to describe these interactions and their effects on bioremediation treatment techniques for organic constituents in a specific situation.

Soil moisture is a significant factor affecting treatment effectiveness of contaminated soil. For example, Sims (1986)⁶ observed more rapid degradation of polynuclear aromatic compounds (expressed as half-life in days) at a soil moisture content of 60 to 80% of field capacity than at a soil moisture content of 20 to 40% as follows: anthracene (37 vs. 43 days), phenanthrene (54 vs. 61 days), and fluoranthene (231 vs. 559 days).

The effect of *temperature* on apparent loss of polycyclic aromatic hydrocarbon (PAH) compounds in a sandy loam soil is summarized in Table 13.7. Temperature has an important effect on the fate and behavior of PAHs and, therefore, has implications for seasonal effects on the rate of biological remediation of soil contaminated with these chemicals. Microbial ecologists have identified ranges of critical environmental conditions that affect aerobic activity of soil microorganisms (Table 13.6). Many of these conditions are controllable and can be modified to enhance activity.

Oxygen may be consumed faster than it can be replaced by diffusion from the atmosphere, and the soil may become anaerobic. Clay content of soil and the presence of organic matter also may affect oxygen content in soil. Clayey soils tend to retain a higher moisture content, which restricts oxygen diffusion, while organic matter may increase microbial activity and deplete

⁵ Ross, D., T.P. Marziarz, and A.L. Bourquin. 1988. Bioremediation of Hazardous Waste Sites in the USA: Case Histories. In: Superfund '88, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 395–397.

⁶ Sims, R.C. 1986. Loading Rates and Frequencies for Land Treatment Systems. In: Land Treatment — A Hazardous Waste Management Alternative, R.C. Loehr, and J.F. Malina (eds.), Water Resources Symposium No. 13, University of Texas Press, Austin, TX, pp. 151–170.

Table 13.6 Critical Environmental Factors for Microbial Activity

Environmental Factor	Optimum Levels
Available soil water	25–85% of water-holding capacity; –0.01 MPa
Oxygen	Aerobic metabolism: >0.2 mg/l dissolved O ₂ ; minimum air-filled pore space of 10% by volume Anaerobic metabolism: O ₂ concentrations < 1% by volume
Redox potential	Aerobes and facultative anaerobes: >50 mV Anaerobes: <50 mV; pH 5.5–8.5
Nutrients	Sufficient nitrogen, phosphorus, and other nutrients, so not limiting to microbial growth (suggested C:N:P ratio of 120:10:1)
Temperature	15–45°C (mesophiles)

Source: Sims and Sims (1991b); compiled from Huddleston et al. (1986), Paul and Clark (1989), Rochkind et al. (1986), and Sims et al. (1984).

available oxygen. Loss of oxygen as a metabolic electron acceptor induces a change in the activity and composition of the soil microbial population. Obligate anaerobic organisms and facultative anaerobic organisms, which use oxygen when it is present or switch to alternative electron acceptors such as nitrate or sulfate in the absence of oxygen, become the dominant populations. Additional information concerning *in situ* anaerobic bioremediation can be found in the document *Handbook on In Situ Treatment of Hazardous Waste-Contaminated Soils* (Chambers et al., 1990/T13.9).

Acclimation of a soil to the presence of a waste is another significant factor affecting bioremediation. Table 13.8 shows this effect for a fossil fuel-contaminated soil. The acclimated soil was exposed to the fossil fuel waste for 1 year before a repeat application of the waste. Results presented in Table 13.8 indicate that a higher percentage of waste was treated in the acclimated soil. Treatment also occurred more rapidly than the treatment in unacclimated soil. Management of contaminated soil, therefore, may include the addition of lightly contaminated, preexposed soil to more heavily contaminated or newly contaminated soil to increase the rate and extent of treatment.

The use of *plants* for stimulating microbial activity in soil results in increased biodegradation of target organic chemicals in contrast to the possibility of vegetative accumulation of chemicals for harvesting and removal from a site. This method has been investigated by Aprill and Sims (1990) and Walton and Anderson (1990).⁷ In soils with low levels of contamination, plant roots may stimulate the biodegradation of toxic chemicals by providing exudates that serve as carbon and energy substrates for soil microorganisms. Aprill and Sims (1990) reported that for soil with initial concentrations of PAHs of approximately 10 to 50 mg/kg, the presence of vegetation in the soil (prairie grasses) resulted in a statistically significant reduction in PAHs, compared with non-vegetated soil.

Measurement of physical abiotic loss mechanisms and partitioning of organic substances into air and soil phases should be used in degradation studies to ensure that generated information is related to disappearance mechanisms of the constituents in the soil system (Abbott and Sims, 1989; Armstrong and Konrad, 1974).⁸ This type of information is needed to more accurately evaluate and select treatment techniques. For example, for organophosphorus pesticides, sorption-catalyzed hydrolysis of ester linkages is known to be an important influence on soil degradation. An understanding of abiotic reactions as influenced by sorption and pH of the system may allow the design of a more effective remediation strategy. If abiotic controls are not used, the disappearance of

⁷Aprill, W. and R.C. Sims. 1990. Evaluation of the Use of Prairie Grasses for Stimulating Polycyclic Aromatic Hydrocarbon Treatment in Soil Chemosphere 20:253–265. Walton, B.T. and T.A. Anderson. 1990. Microbial Degradation of Trichloroethylene in the Rhizosphere: Potential Application to Biological Remediation of Waste Sites. Appl. Environ. Microbiol. 56:1012–1016.

⁸Abbott, C. and R.C. Sims. 1989. Use of Bioassays to Monitor Polycyclic Aromatic Hydrocarbon Contamination in Soil. In: Superfund '89, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 23–26. Armstrong, D.E. and J.G. Konrad. 1974. Nonbiological Degradation of Pesticides. In: Pesticides in Soil and Water, W.D. Guenzi (Ed.), Soil Science Society of America, Madison, WI, chapter 7.

Table 13.7 Effect of Temperature on Degradation of PAHs in a Sandy Loam Soil

Compound	Percent of PAH Remaining			Estimated Half Life (Day) ^a			Half Lives Reported in the Literature (Day)
	10°C	20°C	30°C	10°C	20°C	30°C	
Acenaphthene	5	0	0	<60	<10	<10	96 ^b , 45 ^b , 0.3–4 ^c
Fluorene	8	3	2	60 (+11/–10)	47 (+6/–5)	32 (+5/–3)	65 ^b , 39 ^b , 2–39 ^c
Phenanthrene	36	19	2	200 (+40/–40)	<60	<60	69 ^b , 23 ^b , 26 ^c , 9.7 ^d , 14 ^d
Anthracene	83	51	58	460 (+310/–140)	260 (+160/–70)	200 (+90/–30)	28 ^b , 17 ^b , 108–175 ^c , 17 ^d , 45 ^d
Fluoranthene	94	71	15	^f	440 (+560/–160)	140 (+40/–20)	104 ^b , 29 ^b , 44–182 ^c , 39 ^d , 34 ^d
Pyrene	93	89	43	^f	1900 (+6200/–800)	210 (+160/–60)	73 ^b , 27 ^b , 3–35 ^c , 58 ^d , 48 ^d
Benz[a]anthracene	82	71	50	680 (+300/–160)	430 (+110/–70)	240 (+40/–40)	52 ^b , 123 ^b , 102–252 ^c , 240 ^d , 130 ^d
Chrysene	85	88	86	908 (+520/–270)	1000 (+900/–250)	730 (+370/–180)	70 ^b , 42 ^b , 5.5–10.5 ^c , 328 ^d , 224 ^d
Benzo[b]fluoranthene	77	75	62	580 (+520/–180)	610 (+590/–200)	360 (+150/–80)	73–130 ^e , 85 ^b , 65 ^b
Benzo[k]fluoranthene	93	95	89	910 (+690/–270)	1400 (+3300/–560)	910 (+4400/–410)	143 ^b , 74 ^b
Benzo[a]pyrene	73	54	53	530 (+1700/–230)	290 (+570/–120)	220 (+160/–60)	91 ^b , 69 ^b , 30–420 ^c , 347 ^d , 218 ^d
Dibenz[a,h]anthracene	88	87	83	820 (+1100/–300)	750 (+850/–260)	940 (+12000/450)	74 ^b , 42 ^b , 100–190 ^e
Benzo[g,h,i]perylene	81	76	75	650 (+650/–230)	600 (+570/–190)	590 (+1800/–250)	179 ^b , 70 ^{a,b}
Ideno[1,2,3-c,d]pyrene	80	77	70	600 (+310/–150)	730 (+1100/–270)	630 (+2500/–280)	57 ^b , 42 ^b , 200–600 ^e

^a $t_{1/2}$ (95% confidence interval).

^b T = 20°C Sims (1986).

^c T = 15–25°C Sims and Overcash (1983).

^d T = 20°C PACE (1985).

^e T = 20°C Cims (1982).

^f Least squares slope (for calculations of $t_{1/2}$) = 0 with 95% confidence.

Source: Coover and Sims, 1987.

Table 13.8 Acclimation of Soil to Complex Fossil Fuel Waste

PNA Constituent	Unacclimated Soil		Acclimated Soil	
	Initial Soil Concentration (mg/kg-dry wt)	Reduction in 40 days (%)	Soil Concentration after Reapplication (mg/kg-dry wt) ^a	Reduction in 22 days (%)
Naphthalene	38	90	38	100
Phenanthrene	30	70	30	83
Anthracene	38	58	38	99
Fluoranthene	154	51	159	82
Pyrene	177	47	180	86
Benz(a)anthracene	30	42	40	70
Chrysene	27	25	33	61
Benz(a)pyrene	10	40	12	50

^a First reapplication of waste after 168 days incubation at initial level.

Source: Sims and Sims (1991b), after Sims (1986).

chemicals may be attributed solely to biological activity, though biological activity may not play the major role in the degradation of the chemical. Therefore, knowledge of the reaction mechanism is directly related to efficiency and effectiveness in remediation strategy design and remediation technique selection.

13.4 OTHER TREATMENT APPROACHES

One way to predict and control the rate of transport of a constituent through a subsurface system is to describe its mobility (or relative immobility) by predicting its retardation (Mahmood and Sims, 1986).⁹ Retardation describes the relative velocity of the constituent compared to the rate of movement of water through the subsurface (see Section 4.5 for more information). Retardation in unsaturated soil can be represented as

$$R = 1 + (\rho K_d / \theta) \quad (13.2)$$

where:

ρ = soil bulk density

K_d = soil–water partition coefficient (Section 4.5.2)

θ = volumetric moisture content

For a saturated system, θ is replaced by the porosity of the system.

This information can be used to evaluate treatment techniques for a contaminated soil system (e.g., techniques to modify the soil–water partition coefficient, such as control of soil moisture, changes in bulk density, or addition of amendments to the soil). Constituents can be “captured” or contained within the system by using these techniques, thus allowing time for degradation at the site or for engineering implementation and performance of other remediation treatment techniques, such as soil washing (Sims et al., 1989/T13.9).

13.4.1 Sorption, Ion Exchange, and Precipitation

Constituents in *in situ* and prepared bed treatment systems are generally immobilized through sorption, ion exchange, and precipitation reactions. These techniques reduce the rate of contaminant

⁹ Mahmood, R.J. and R.C. Sims. 1986. Mobility of Organics in Land Treatment Systems. *Journal of Environmental Engineering* (ASCE) 112:236–245.

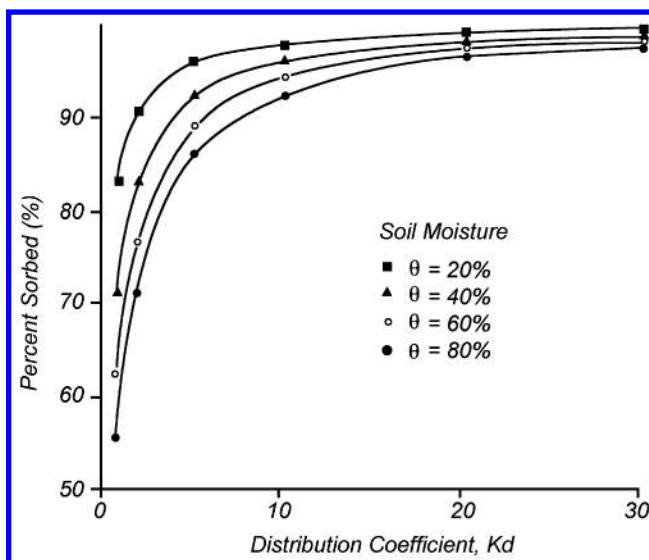


Figure 13.8 Sorption of chemicals to soil as a function of soil moisture content and partition coefficient K_d (Sims and Sims, 1991b, after Sims et al., 1986).

release from the soil environment so that concentrations along exposure pathways are held within acceptable limits. The effects of moisture and the distribution coefficient, K_d , on immobilization are illustrated in Figure 13.8. Results indicate that for chemicals with K_d values less than 10, management of soil moisture is important with regard to immobilizing chemicals; for chemicals with K_d values greater than 10, management of soil moisture is less important. Approaches for controlling soil moisture include run-on and runoff controls, temporary capping or covering, and irrigation scheduling.

The cation exchange capacity (CEC) of soil also can be evaluated with regard to organic as well as metal immobilization. Positively charged organic chemicals and metals will generally readily attach to soil materials with negatively charged functional groups and negatively charged clay particles. Addition of clays, synthetic resins, and zeolites will increase the CEC of soils and increase immobilization of chemicals sensitive to CEC characteristics of a soil (Sims et al., 1984/T13.9). For inorganic chemicals that are negatively charged in soil systems and can exist in several oxidation states (e.g., chromium, selenium, and arsenic), immobilization, as well as the toxic form of the chemical, may potentially be controlled by managing the redox and pH of the soil system. Management of redox and pH may be short-term or long-term, depending upon the goals of site management (e.g., temporary immobilization while delivery and recovery systems are designed and implemented, followed by soil flushing with aqueous or surfactant solutions for removal and recovery of the contaminants).

13.4.2 Solidification and Stabilization

Solidification and stabilization are additional immobilization techniques that are applicable to *in situ* and prepared bed systems. These techniques are designed to accomplish one or more of the following: (1) production of a solid from a liquid or semisolid waste, (2) reduction of contaminant solubility, and (3) a decrease in the exposed surface area across which transfer may occur. Solidification may involve encapsulation of fine waste particles (microencapsulation) or large blocks of waste (macroencapsulation). Stabilization refers to the process of reducing the hazardous potential of waste materials by converting contaminants into their least soluble, mobile, or toxic form (Chambers et al., 1990/T13.9). A milestone publication providing additional detail on this technique

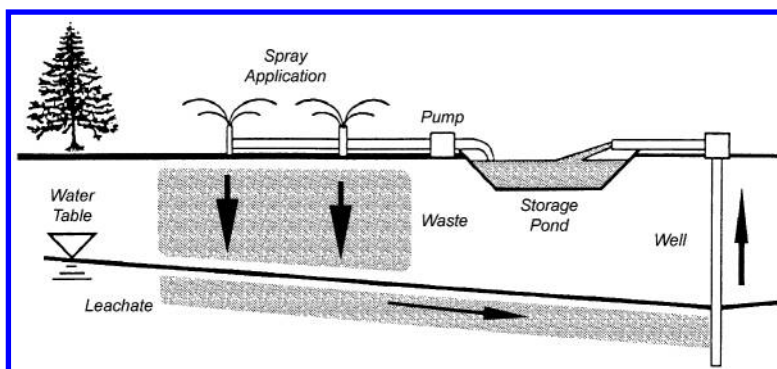


Figure 13.9 Schematic of soil flushing and recycle system (U.S. EPA, 1990).

is the *Handbook for Stabilization/Solidification of Hazardous Wastes* (Cullinane et al., 1986/T13.9). [Table 13.3](#) summarizes some information of fixation and capsulization methods for stabilizing contaminated soils.

Systems for delivering reagents to the contaminated area include (1) injection systems, (2) soil surface applicators, and (3) delivery and application of electrical energy for melting soils and rocks that contain hazardous materials. Equipment required for preparing, mixing, and applying reagents depends upon the reagent, process, and depth of contamination (Chambers et al., 1990/T13.9).

Important parameters identified by Truett et al. (1983/T13.9) for solidification and stabilization of hazardous wastes include (1) reagent viscosity, (2) permeability of soils, (3) porosity of waste materials and soil, (4) distribution of waste in surrounding material (rocks, soils, etc.), and (5) rate of reaction. The most significant challenge in applying solidification/stabilization treatment *in situ* is achieving uniform mixing of added chemical agent(s) with the contaminated soils (Chambers et al., 1990/T13.9). Design factors involve delivery and mixing systems to obtain complete and uniform distribution of added reagent throughout the contaminated soil (U.S. EPA, 1990).

13.4.3 Soil Flushing

Mobilization of organic and inorganic contaminants from soil may be accomplished using soil flushing and recovery and treatment of the elutriate. Flushing solutions generally include water, acidic and basic solutions, surfactants, and solvents. The solutions partition a contaminant into the liquid phase through the volume of added liquid or by decreasing the distribution coefficient between the soil and the flushing phase (Sims et al., 1984/T13.9; Raghavan et al., 1990/T13.9). A schematic of a soil flushing system is shown in Figure 13.9. Components consist of (1) the flushing solution, and (2) delivery and recovery systems, which may include injection and recovery wells, equipment for surface applications, and holding tanks for storing elutriate for reapplication.

Variables affecting application of the technique include (1) concentration and volume of contamination, (2) distribution coefficients of waste constituents, (3) interactions of flushing solutions with soil, and (4) suitability of site for installation of wells, drains, etc., for delivery and recovery. Design factors include sizing the delivery and recovery systems to ensure complete recovery of the elutriate. Problems with respect to flushing of bulk fluids, or NAPLs, from soil systems are due to the following characteristics of bulk fluids: (1) low water solubility, (2) high interfacial tension, and (3) poor relative permeability. Relative permeability is defined as

$$M = [K_d/U_d]/[K_o/U_o] \quad (13.3)$$

where:

M = mobility ratio

K_d = fluid permeability (water)

K_o = oil permeability

U_d = viscosity of fluid (water)

U_o = viscosity of oil

Strategies for flushing of bulk liquids from soil generally involve control of one or more of the variables affecting the mobility ratio through adding chemicals to decrease mobility of water or increase mobility of oil (e.g., adding surfactants or steam to decrease U_o or adding polymers to increase U_d).

Use of soil flushing in a treatment train with bioremediation has been evaluated by Dworkin et al. (1988) for a wood preserving contaminated site.¹⁰ Flushing using surfactant–polymer combinations was used to remove high concentrations of PAH compounds; residual low concentrations were treated using biological processes. Mahmood and Sims (1985)¹¹ found that when methanol was used as the solvent in a soil system to flush PAHs from a soil, the resultant concentration of the PAHs in the solution phase was several orders of magnitude higher than the concentration of the PAHs in water.

13.4.4 Soil Thermal Extraction Methods

Mobilization and extraction of subsurface organic contaminants can be enhanced with the addition of heat energy. The addition of heat to the subsurface is intended to increase the partitioning of organic chemicals into the vapor phase where they may be more readily drawn from the subsurface using conventional vapor extraction technologies. Several methods are currently employed to heat the subsurface: conductive heating, radio frequency heating (see Section 14.6.1), steam flooding, and electrical resistivity heating (Looney and Falta, 2000/T13.9).

Conductive heating creates high temperatures in the subsurface by the insertion of rods containing resistive heaters. Reed and Conley (2000/T13.9) provide an overview of conductive heating technology used to remove organic contaminants from the subsurface. Heat is conducted through the surrounding soil as heat is radiated outward through the rods. This process is capable of generating heat in excess of 500°C near the rods. In the presence of oxygen, organic contaminants can be destroyed at these high temperatures. Conductive heating has also been called *in situ* thermal destruction and has been used to remove free-phase NAPLs in the vadose or saturated zones.

The injection of steam into the subsurface can be an effective removal technology for organic sources in the vadose zone. There are several mechanisms that have been identified accounting for the removal of contaminants through the injection of steam. Compounds with low boiling points and high vapor pressures are easily vaporized. The evaporation rate of semivolatiles is also enhanced due to the increased temperature. Contaminated water as well as nonaqueous phase liquids can be displaced by the condensation front of the advancing steam. Another removal mechanism of steam and other thermal technologies is desorption of organic compounds from soil solids due to the elevated temperature. Finally, once the steam injection has terminated, continued vacuum extraction has been shown to provide high recovery rates to compounds that were not exposed to the steam front (Udell and Stewart, 1989/T13.9). Falta (2000/T13.9) provides a thorough review of current steam technology as applied to remediation, including discussion of physical process, energy delivery, contaminant removal, and field studies.

¹⁰ Dworkin, D., D.J. Messinger, and R.M. Shapot. 1988. In Situ Flushing and Bioreclamation Technologies at a Creosote-Based Wood Treatment Plant. In: Proc. 5th National Conference on Hazardous Wastes and Hazardous Materials, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 67–78.

¹¹ Mahmood, R.J. and R.C. Sims. 1985. Enhanced Mobility of Polynuclear Aromatic Compounds in Soil Systems. In: Proc. 1985 Environmental Engineering Specialty Annual Conference (Boston, MA), American Society of Civil Engineers, pp. 128–135.

Another method of providing heat to the subsurface for removal of organic compounds is through electrical resistivity heating. Electrical resistivity heating can raise the temperature in the subsurface to that of boiling water, which creates an *in situ* source of steam for stripping of volatile organic compounds. Conventional soil vapor extraction techniques are then used to remove the mobile vapors. Electrical resistivity relies on generating a current in the subsurface using electrodes. The heating rate is equivalent to the power dissipated in the subsurface, and heating increases as current flow increases. The configuration of electrodes is critical to creating a uniform distribution of heat. The optimum configuration relies on six metal electrodes placed in a circle around a central neutral electrode (Heath, 2000/T13.9). The applied voltage can be adjusted in the field to provide the current necessary to induce resistive heating at the rate needed for remediation. Six-phase soil heating was developed by Battelle Memorial Institute as a method to enhance the removal of volatile organic compounds from soils with low permeability.

13.5 PREPARED BED REACTORS

The previous sections have focused on *in situ* soil treatment methods. In a prepared bed system, the contaminated soil may be either (1) physically moved from its original site to a newly prepared area, which has been designed to enhance remediation and prevent transport of contaminants from the site, or (2) removed from the site to a storage area while the original location is prepared for use, and then returned to the bed, where the treatment is accomplished. Preparation of the bed may include placement of a clay or plastic liner to retard transport of contaminants from the site or addition of uncontaminated soil to provide an additional treatment medium.

Table 13.1 and Table 13.2 identify possible prepared bed reactor technologies and provide information on function as well as application and limitations. Treatment of contaminants with a prepared bed may be based on the techniques previously identified and described for *in situ* treatment. An example of the use of a prepared bed reactor for soil remediation was described by Lynch and Genes (1989).¹² Prepared bed treatment of creosote-contaminated soils from a shallow, unlined surface impoundment was demonstrated at a disposal facility for a wood preserving operation in Minnesota. The contaminated soils contained creosote constituents consisting primarily of PAHs at concentrations ranging from 1000 to 10,000 ppm. Prior to implementation of the full-scale treatment operation, bench-scale and pilot-scale studies simulating proposed full-scale conditions were conducted to define operation and design parameters. Over a 4-month period, 62 to 80% removal of total PAHs was achieved in all test plots and laboratory reactors. Two-ring PAH compounds were reduced by 80 to 90%, three-ring PAHs by 82 to 93%, and four-ring (or more) PAHs by 21 to 60%.

The full-scale system involved preparation of a treatment area within the confines of the existing impoundment. A lined waste pile for temporary storage of the sludge and contaminated soil from the impoundment was constructed. All standing water from the impoundment was removed, and the sludges were excavated and segregated for subsequent free oil recovery. Three to 5 ft of visibly contaminated soil was excavated and stored in the lined waste pile. The bottom of the impoundment was stabilized as a base for the treatment area. The treatment area was constructed by installation of a polyethylene liner, a leachate collection system, 4 ft of clean backfill, and the addition of manure to achieve a carbon:nitrogen ratio of 50:1. A sump for collection of storm water and leachate and a center pivot irrigation system also were installed. The lined treatment area was required because natural soils at the site were highly permeable. A cap also was needed for residual contaminants left in place below the liner. Contaminated soil was periodically applied to the treatment facility and rototilled into the treatment soil. Soil moisture was maintained near field capacity with the irrigation system. During the first year of operation, greater than 95% reductions

¹² Lynch, J. and B.R. Genes. 1989. Land Treatment of Hydrocarbon Contaminated Soils. In: Petroleum Contaminated Soils, Vol. 1: Remediation Techniques, Environmental Fate, and Risk Assessment, P.T. Kostecki and E.J. Calabrese (Eds.), Lewis Publishers, Chelsea, MI, pp. 163–174.

in concentration were obtained for two- and three-ring PAHs. Greater than 70% of four- and five-ring PAH compounds were degraded during the first year. Comparison of half-lives of polynuclear aromatics (PNAs) in the full-scale facility were in the low end of the range of half-lives reported for the test plot units. Only two PNA compounds were detected in drain tile water samples, at concentrations near analytical detection limits.

Prepared bed treatment of a Texas oil field site with storage pit backfill soils contaminated with styrene, still bottom tars, and chlorinated hydrocarbon solvents was demonstrated on a pilot scale (St. John and Sikes, 1988).¹³ The remediation efforts included biological, chemical, and physical treatment strategies. The pilot-scale, solid-phase biological treatment facility consisted of a plastic film greenhouse enclosure, a lined soil treatment bed with an underdrain, an overhead spray system for distributing water, nutrients, and inocula, an organic vapor control system consisting of activated carbon absorbers, and a fermentation vessel for preparing microbial inoculum or treating contaminated leachate from the backfill soils. Soils were excavated from the contaminated area and transferred to the treatment facility. Average concentrations of volatile organic compounds (VOCs) were reduced by more than 99% during the 94-day period of operation of the facility; most of the removal was attributed to air stripping. Biodegradation of semivolatile compounds reduced average concentrations by 89% during the treatment period.

13.6 GUIDE TO MAJOR REFERENCES

Table 13.9 provides an index to major references on soil treatment and remediation, including (1) general reviews, (2) soil treatability studies, (3) soil cleanup standards, (4) petroleum/hydrocarbon contaminated soils, (5) contaminated sediments, and (6) radioactive contamination. Major references on the following treatment categories are also indexed in Table 13.9: (1) in-place treatment, (2) bioremediation, (3) stabilization/solidification, and (4) soil vapor extraction and other specific methods.

Table 12.7 provides an index to major references that address broader aspects of remediation of contaminated soil and ground water. Especially note the Battelle contaminated sediment, bioremediation and chlorinated/recalcitrant compounds volumes that are listed in that table. Currently, many remedial techniques are being used and evaluated for cleanup of contaminated soils.

From 1992 to 2002 the U.S. EPA Technology Innovation Office published a newsletter titled *Tech Trends*, which provided information on innovative soil remediation technologies. See Section 12.5, which provides information on the successor newsletter, and also information on various documents that are available as part of U.S. EPA's Superfund Innovative Technology Evaluation (SITE) program.

¹³ St. John, W.D. and D.J. Sikes. 1988. Complex Industrial Waste Sites. In: Environmental Biotechnology — Reducing Risks from Environmental Chemicals through Biotechnology, G.S. Omenn (Ed.), Plenum Press, New York, NY, pp. 237–252.

Table 13.9 Index to Major References on Soil Treatment and Remediation

Topic	References
General Reviews	Chen (1999), Galer (1988), Looney and Falta (2000), Sims et al. (1984), U.S. EPA (1988b — technology screening guide, 1989a, 1990), Wise and Trantolo (1994), Wise et al. (2000b), Yong (2002), see generally the soil and ground water references and conference and symposium series in identified in Table 12.7; <u>Innovative Technologies</u> : U.S. EPA (1999/T12.7), Wilson and Clark (1993)
Soil Treatability Studies	Loehr (1989), McGinnis et al. (1988 — creosote/PCP), Sims et al. (1986, 1988), see also treatability references in Table 12.7
Soil Cleanup Standards	Booz, Allen & Hamilton (1989), Buonicore (1996/T12.7), Fitchko (1989), Hwang et al. (1987), Lipsky et al. (1989), Oliver et al. (1993/T12.7), U.S. EPA (1989b, 1994b, 1996a, 1996b), WEF (1994a/T12.7)
Petroleum/Hydrocarbon Contaminated Soils	Fiorenza et al. (1999 — phytoremediation), Nash et al. (1992), Riser-Roberts (1998), von Fahnstock and Wickramanayake (1998 — biopiles), see also petroleum/hydrocarbon contaminated soil conference series and UST/spill remediation references in Table 12.7
Contaminated Sediments	Fitchko (1989), Voskuil (1991), Wilson (1988 — PCB), see also Battelle contaminated sediment remediation conference series
Radioactive Contamination	Oh (2001), U.S. EPA (1988a, 1990a), Voskuil (1992)
Treatment Methods (also see references listed in Table 12.7 on hazardous waste treatment)	
In-Place Treatment	Chambers et al. (1990), DiGuilio (1992 — soil venting), Siegrist et al. (2001 — chemical oxidation), Sims et al. (1984), Unterberg (1987 — wet-air oxidation), U.S. EPA (1986), Wilson (1995); <u>Explosives</u> : Spain et al. (2000), Ward (2000); <u>Heavy Metal Contamination</u> : Czupyma et al. (1989), Iskander (2001), Testa and Conka (2000); <u>Soil Flushing/Washing</u> : Nash (1987), Raghavan et al. (1990), Ward (2000); <u>Passive Soil Vapor Extraction</u> : Looney and Falta (2000), Rossabi (1999), Rossabi et al. (1994), Zachary, (1993), Zwick et al. (1994); <u>Thermal Enhancements</u> : Balshaw-Biddle et al. (1999), Looney and Falta (2000), Lowe et al. (1999 — SVE), Udell and Stewart 1989, U.S. EPA (1995), Wickramanayake and Gavaskar (2000), see also Table 12.7
Bioremediation	Leeson and Hinchee (1997 — bioventing), Sims et al. (1989, 1993), Wise et al. (2000a), see also references on soil and ground-water bioremediation in Table 12.7
Physical/Chemical	U.S. EPA (1994a)
Stabilization/Solidification	Arozarena et al. (1989), Battelle (1993), Cullinane et al. (1986), Means et al. (1994), Truett et al. (1983), U.S. EPA (1979, 1980, 1986, 1990b, 1999), Voskuil (1992 — vitrification)

Table 13.9 References (Appendix F contains references for figure and table sources.)

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* See Preface for information on how to obtain documents from CERL and NTIS.

Remediation of Contaminated Ground Water

14.1 OVERVIEW

Restoration of contaminated ground water to former background or near-background conditions is generally accomplished through one of two overall approaches. One approach involves natural or induced *in situ* treatment; the other uses engineered systems for the removal of ground water and is usually followed by treatment. For both approaches to ground-water restoration, any source that continues to contaminate ground water in the zone to be restored must be removed, isolated, or concurrently treated. In the former approach, treatment or removal of a still existing contamination source may eventually restore ground-water quality through natural processes. In other situations, contaminated ground water is removed from the aquifer or discharged to a surface water, and natural replacement is relied upon to eventually restore ground-water quality. Typically, however, these processes in the ground-water system take many years, decades, or even centuries. As a result, ground-water restoration typically requires approaches involving ground-water removal and treatment or, if necessary, induced *in situ* treatment following source control (removal, isolation, treatment). Site-specific conditions, properly defined and understood, provide ground-water engineers with the basic background information for determining an effective approach and for selecting and designing a cost-effective ground-water restoration system appropriate to the site.

This chapter provides an overview of aquifer restoration technologies utilizing techniques derived from interrelated disciplines of hydrology, geochemistry, civil engineering, construction, biology, and agronomy. Many of the technologies have been developed by demonstration and research in conjunction with remedial activities in the Superfund program. [Figure 14.1](#) presents three general response actions and process options for a ground-water remediation program from a management viewpoint. The components of an *active restoration* response include the removal and treatment of contaminated ground water, the discharge of the treated water, and institutional controls. The *containment response* option includes the monitoring and containment of the contaminated ground water as well as institutional controls. The *natural attenuation response* includes institutional controls and monitoring. This chapter, which focuses on the technical aspect of remediation, briefly discusses the extraction and treatment components of active restoration and containment. The major emphasis of the chapter is on ground-water pumping systems and *in situ* biological treatment for organic contaminants that are found at almost all hazardous waste sites. [Table 14.1](#) lists technologies that are discussed in this chapter.

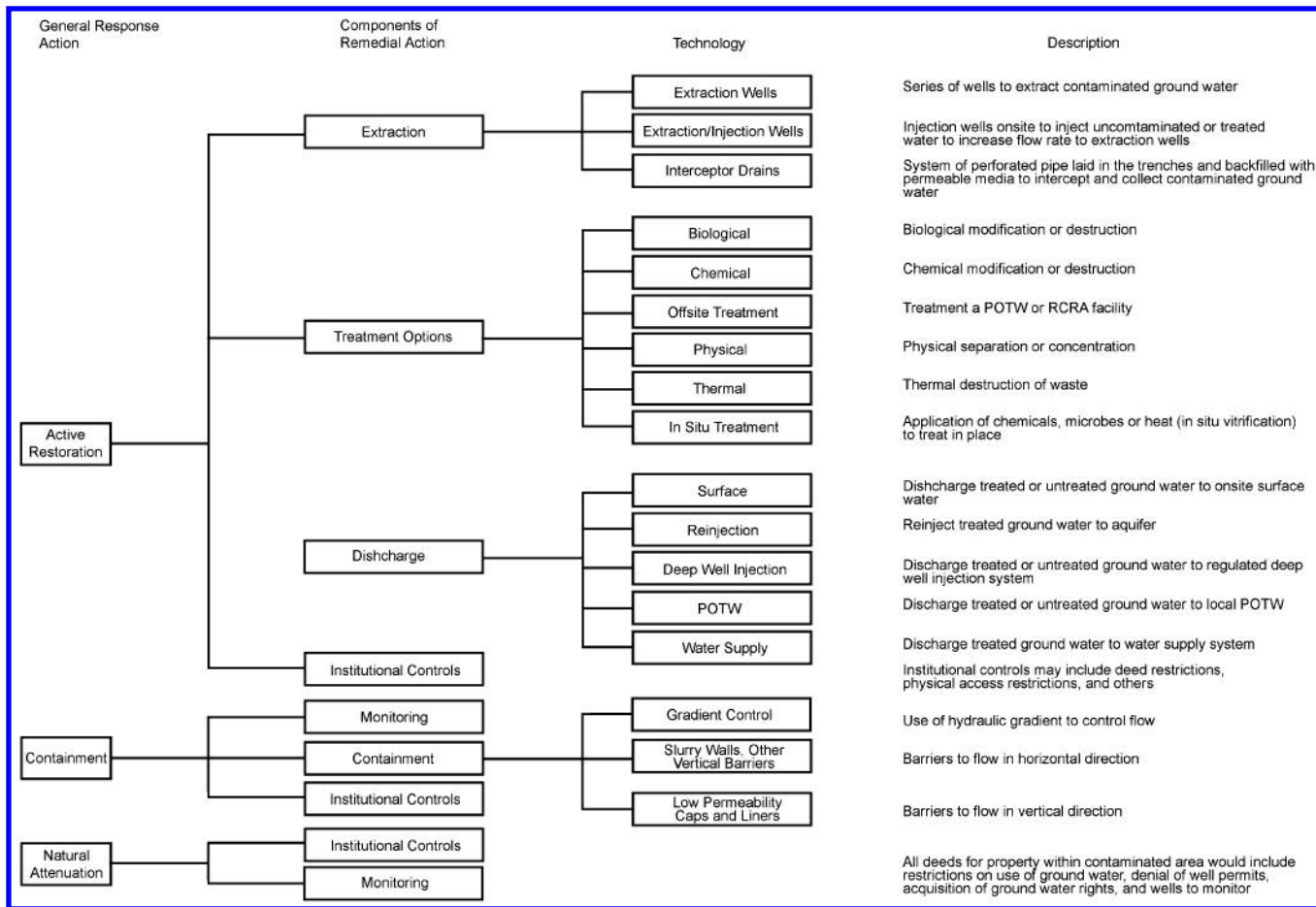


Figure 14.1 General response actions and process options for ground water (U.S. EPA, 1988b).

Table 14.1 Available Technologies for Ground Water Containment and Restoration

Ground-Water Source Containment and Isolation

Removal ([Section 14.2.1](#))
Surface water control ([Section 14.2.2](#))
Barriers ([Sections 14.3.1 to 14.3.3](#))
Hydrodynamic control ([Section 14.3.5](#))

Ground-Water Collection and Removal

Pumping ([Section 14.4.1](#))
Drains ([Section 14.4.2](#))

Ground-Water Treatment

Physical ([Section 14.5.1](#))
Chemical ([Section 14.5.2](#))
Biological ([Section 14.5.3](#))
In situ treatment ([Section 14.6](#))

14.1.1 Site Characterization

Ground-water restoration activities require dedication of sufficient resources to collect and understand background information. Field data provide detailed information about the hydrology and geochemistry of the site, as well as the types of contaminants to be removed, their concentrations, and distribution. Monitoring well construction (Section 9.3), ground-water sampling (Section 9.5), and contaminant behavior (Chapter 4) are important elements of site definition that allow the restoration program to be planned and implemented. Understanding the ground-water flow at the site is important in developing the restoration plan. A literature review to determine the characteristics of the contaminants is also useful in selecting restoration techniques best suited to the site. Finally, laboratory studies, including treatability studies, sorption isotherms, and column and microcosm studies to determine contaminant transport and transformation parameters assist in developing a full understanding of the site conditions and potential alternatives for ground-water remediation.

14.1.2 Treatment Trains

In most contaminated hydrogeologic systems, the remediation process may be so complex, in terms of contaminant behavior and site characteristics, that no one system or unit is capable of meeting all requirements. Consequently, several unit operations are often combined in series and sometimes in parallel to effectively restore ground-water quality to the required level. Barriers and hydrodynamic controls may serve as temporary plume control measures; however, hydrodynamic processes are integral parts of any withdrawal and treatment or *in situ* treatment process.

Most remediation projects are typically started by removing the source. The next step may be the installation of pumping systems to remove free product floating on the water surface or the removal of soluble contaminants for treatment at the surface. Barriers might also be constructed to slow an advancing plume or to reduce the amount of water requiring treatment. Enhanced bioremediation techniques may be feasible in some of the more diluted areas of the plume. In some circumstances, a site may reach final restoration goals using natural chemical and biological processes. An adequate monitoring program would be required to establish data on the progress of the restoration program.

Steps in treatment of contaminated ground water include the removal, collection, and delivery of the contaminated water to the treatment units, and in the case of *in situ* processes, delivery of the treatment materials to the contaminated areas in the aquifer. A thorough knowledge and

understanding of the hydrogeologic and geochemical characteristics of the site are required to design a system that will optimize the remediation techniques selected, maximize the predictability of restoration effectiveness, and allow for the development of a cost-effective and lasting remediation program.

14.1.3 Regulatory Considerations

The principal criteria for selecting remediation procedures are the water quality level to which to restore an aquifer and the most economical technology available to reach that level. Institutional limitations, however, sometimes override these criteria in determining if, when, and how remediation will be selected and carried out.

Response to a ground-water contamination problem is likely to require compliance with several local, state, and federal pollution control laws and regulations. If the response involves handling hazardous wastes, discharging substances into the air or surface waters, or injecting wastes underground, federal and state pollution control laws will apply. These laws do not exempt the activities of federal, state, or local officials or other parties attempting to remediate contamination problems. They apply to both generators and responding parties, and it is not unusual for these pollution control laws to conflict. A hazardous waste remediation project must meet RCRA permit requirements governing the transport and disposal of hazardous wastes, which can influence the selection of the remediation plan and the scheduling of cleanup activities.

In situ remediation procedures may be subject to permitting or other requirements under federal or state underground injection control programs. Withdrawal and treatment approaches may be subject to regulation under federal or state air pollution control programs or to pretreatment requirements if contaminated ground water is to be discharged to a surface water or to a municipal wastewater treatment system. A remediation plan involving pumping from an aquifer may be subject to state ground-water regulations on well construction and well spacing, and may need to consider various competing legal rights to extract ground water. U.S. EPA's *CERCLA Compliance with Other Laws Manual: Interim Final* (EPA/540/G-89/006) identifies major laws and regulations that must be considered.

Other factors influencing selection and design of a ground-water remediation program include the availability of alternative sources of water supply, political and judicial constraints, and the availability of funds. Where alternate water supplies are plentiful and economical, there may not be a demand for total remediation; adequate remediation to protect human health and the environment may be sufficient. In the final analysis, responsible agencies can pursue remediation measures to the extent that resources are made available.

14.2 SOURCE CONTROL

The objective of source control strategies is to reduce or eliminate the volume of waste, thereby eliminating or minimizing ongoing contamination of the ground-water environment. Source control techniques include removal of the source, surface water controls, ground-water barriers, interceptors, and hydrodynamic controls. [Table 14.2](#) lists these commonly used source control technologies and the advantages and disadvantages of each. A brief discussion of each technique follows.

14.2.1 Removal

Soil and water from a hazardous waste site may be removed for treatment or relocation to a site that is more acceptable from an engineering or environmental viewpoint. While the removal and reburial of contaminated materials at a more controlled site appears to solve the contamination problem, various factors need to be evaluated before excavation commences. These factors include

Table 14.2 Advantages and Disadvantages of Commonly Used Source Control Technologies

Method	Advantages	Disadvantages
Source Removal		
	<ul style="list-style-type: none"> Source is moved to controlled environment 	<ul style="list-style-type: none"> Site accessibility often difficult Potential for accidents during transport High costs
Surface Water Controls		
Changing contours and runoff and run-on characteristics	<ul style="list-style-type: none"> Relatively inexpensive Reduces amount of potential infiltration; allows for drainage while controlling erosion 	<ul style="list-style-type: none"> Requires maintenance to repair slopes and eliminate depressions
Capping	<ul style="list-style-type: none"> Prevents or minimizes infiltration Can be used at almost any site 	<ul style="list-style-type: none"> Requires long-term maintenance
Revegetation (used with capping and contouring)	<ul style="list-style-type: none"> Reduces erosion 	<ul style="list-style-type: none"> Roots may penetrate cap allowing for infiltration Requires maintenance
Ground-Water Barriers		
Slurry trench wall	<ul style="list-style-type: none"> Construction methods are simple Adjacent areas are not affected by ground-water drawdown Bentonite (mineral) will not deteriorate with age Leachate-resistant bentonites are available Low maintenance requirements Eliminates risks due to strikes, pump breakdowns, or power failures Eliminates headers and other aboveground obstructions 	<ul style="list-style-type: none"> Cost of shipping bentonite to some areas of the country is high Some construction procedures are patented and require a license Overexcavation in rocky ground is necessary because of boulders Bentonite deteriorates when exposed to high-ionic-strength leachate Adequate key to impermeable formation is critical Difficult to assess in-place integrity
Grouting	<ul style="list-style-type: none"> When designed on the basis of thorough preliminary investigations, grouts can be very successful Grouts have been used over 100 years in construction and soil stabilization projects Many kinds of grout available to suit a wide range of soil types 	<ul style="list-style-type: none"> Grouting is limited to granular types of soils having a pore size large enough to accept grout fluids under pressure, yet large enough to prevent significant pollutant migration before implementation Grouting in a highly layered soil profile may result in incomplete formation of a grout envelope Presence of high water table and rapidly flowing ground water limits groutability through extensive transport of contaminants and rapid dilution of grouts Some grouting techniques are proprietary Procedure requires careful planning and pretesting; methods of ensuring that all voids in the wall have been effectively grouted are not readily available Grouts may not withstand attack from specific pollutants
Sheet piling	<ul style="list-style-type: none"> Construction is not difficult and no excavation is necessary Contractors, equipment, and materials are available throughout the U.S. Construction can be economical No maintenance required after construction 	<ul style="list-style-type: none"> Steel sheet piling initially is not watertight Driving piles through ground containing boulders is difficult Certain chemicals may attack the steel

Table 14.2 Advantages and Disadvantages of Commonly Used Source Control Technologies (*Continued*)

Method	Advantages	Disadvantages
Interceptor Systems		
	<ul style="list-style-type: none"> • Easy and inexpensive to install • Useful for intercepting landfill side seepage and runoff • Useful for collecting leachate in poorly permeable soils • Large wetted perimeter allows for high rates of flow • Possible to monitor and recover • Produces much less fluid to be handled than well point system (hydrodynamic controls) 	<ul style="list-style-type: none"> • When dissolved constituents are involved it may be necessary to monitor ground water downgradient of the recovery line • Open systems require safety precautions to prevent fires or explosions • Interceptor trenches are less efficient well point systems (hydrodynamic controls) • Operation and maintenance costs are high • Not useful for deep disposal sites
Hydrodynamic Controls		
	<ul style="list-style-type: none"> • Less costly to construct than physical barriers • High degree of flexibility in design; additional wells can be added • Efficient and effective means of assuring ground-water pollution control • Previously installed monitoring wells can sometimes be employed • Can sometimes include recharge of aquifer as part of the strategy • Can be installed readily 	<ul style="list-style-type: none"> • High operation and maintenance costs • High cost of monitoring the system • Withdrawal systems necessarily remove clean (excess) water along with polluted water • Some systems require the use of sophisticated mathematical models to evaluate effectiveness • Withdrawal systems will usually require surface treatment prior to discharge • Applications to fine soils is limited • System failures due to breakdown or power failures may lead to contaminant movement

Source: Compiled from U.S. EPA (1985), Knox et al. (1984), Nielsen (1983), and Wagner et al. (1986).

the excavation and handling of bulky partially decomposed or hazardous waste; the distance and means of transportation to the reburial site; the risks to public health and the environment on the route between sites; political, social, and economic factors associated with locating a new site; the disposal of the contaminated ground water at the sites; the control of nuisances and vectors during excavation; reclamation of the excavated site; and the costs involved (Tolman et al., 1978/T14.9). These considerations suggest that excavation and relocation may be a viable alternative only where costs are not significant compared to the importance of the resource protection. In some cases, removal and reburial in an approved facility transfers a problem from one location to another, and possibly creates additional problems.

14.2.2 Surface Water Controls

Surface water control measures are used to minimize the infiltration and percolation of surface water or precipitation into the ground water of a waste site. This can be accomplished by contouring the site, providing a cap or barrier to infiltration, and revegetating the site.

Changing Contours. Several standard engineering techniques can be used to change the contour and runoff or run-on characteristics of a particular site. Some of the more common techniques are dikes and berms, ditches, diversion waterways, terraces, benches, chutes, downpipes, levees, seepage basins, sedimentation basins, and surface grading.

Capping. A cover or cap of low-permeable material prevents water from entering the site, thus reducing leachate generation. Covers also can control vapors or gases produced in a landfill. Covers or caps may be constructed of native soils, clays, synthetic membranes, soil cement, bituminous concrete, or asphalt.

Revegetation. Revegetation can be a cost-effective method of stabilizing the surface of a waste site, especially when preceded by capping and contouring. Vegetation reduces raindrop impact and runoff velocity and strengthens the soil mass, thereby reducing erosion by wind and water. It also improves the site aesthetically.

14.3 CONTAINMENT: GROUND-WATER BARRIERS AND FLOW CONTROL

Subsurface barriers are designed to prevent or control ground-water flow into, through, or from a certain location. Barriers keep fresh ground water from coming into contact with a contaminated aquifer zone or ground water from existing areas of contamination from moving into areas of clean ground water. The types of barriers commonly used are included in [Table 14.2](#) and are described further in the following section.

14.3.1 Slurry Trench Wall

Slurry trench walls are placed either upgradient from a waste site to prevent flow of ground water into the site or around a waste site to prevent the movement of contaminated ground water away from it. A slurry wall may be keyed in to a low-permeability confining layer by extending partway into the confining layer, or it may extend several feet into the water table to act as a barrier to floating contaminants. A slurry trench wall is constructed by excavating a trench at the proper location and to the desired depth, while keeping the trench filled with a clay slurry composed of a 5 to 7% by weight suspension of bentonite in water. The slurry maintains the vertical stability of the trench walls by exerting a hydrostatic pressure against the surrounding ground water and also forms a low-permeability filter cake on the walls of the trench. As the slurry trench is excavated, it is simultaneously backfilled with a material that forms the final wall. The three major types of slurry backfill mixtures are soil bentonite, cement bentonite, and concrete.

Slurry trench walls are reported to have a reasonable service life and short construction time, cause minimal environmental impact during construction, and be a highly cost-effective method for enclosing large areas under certain conditions (Nielsen, 1983/T14.9). A concern regarding the use of a slurry wall where contaminated materials are in direct contact with the wall is the long-term integrity of the wall (Wagner et al., 1986a/T12.7). In such cases, the condition of the wall needs to be verified over time by ground-water monitoring.

14.3.2 Grouting

Grouting is the process of injecting stabilizing materials under pressure into subsurface soils or rocks to fill and thereby seal the voids, cracks, fissures, or other openings. *Grout curtains* are fixed, underground physical barriers formed by injecting grout through tubes. The amount of grout needed is a function of the available void space, the density of the grout, and the pressures used in setting the grout; however, two or more rows of grout are normally required to provide a good seal. The grout used may be either particulate (i.e., Portland cement) or chemical (i.e., sodium silicate) depending on the soil type and the contaminant present. Grouting creates a fairly effective barrier to ground-water movement, although the degree of completeness of the grout curtain is difficult to ascertain (Nielsen, 1983/T14.9). Incomplete penetration of the grout into the soil voids would increase the permeability of the curtain.

Semicircular grout curtains provide the most complete containment but require that the grouting take place in contaminated ground water downgradient of the source (Wagner et al., 1986a/T12.7).

A variation of the grout curtain is the *vibrating beam technique* for placing thin (approximately 4 in.) curtains or walls. Although this type of barrier is sometimes called a slurry wall, it is more closely related to a grout curtain since the slurry is injected through a pipe in a manner similar to

that of grouting. A suspended I-beam connected to a vibrating driver-extractor is vibrated through the ground to the desired depth. As the beam is raised at a controlled rate, slurry is injected through a set of nozzles at the base of the beam, filling the void left by the beam's withdrawal. The vibrating beam technique is most efficient in loose, unconsolidated deposits such as sands and gravels.

Another method that uses grouting is *bottom sealing*, where grout is injected through drill holes to form a horizontal or curved barrier below the site to prevent downward migration of contaminants.

Block displacement is a relatively new plume management method, in which a slurry is injected so that it forms a subsurface barrier around and below a specific mass or "block" of material. Continued pressure injection of the slurry produces an uplift force on the bottom of the block, resulting in a vertical displacement proportional to the slurry volume pumped.

14.3.3 Sheet Piling, Membrane, and Synthetic Sheet Curtains

Sheet piling cutoff walls can be made of wood, reinforced concrete, or steel, with steel being the most effective material for constructing a ground-water barrier. The construction of a sheet pile cutoff wall involves driving lengths of steel sheets through unconsolidated materials with a pile driver. The individual sheet piles are connected along the edges with various types of interlocking joints, which can provide permeable pathways for ground-water movement if they do not become watertight naturally. It may be desirable to fill these joints with an impermeable material such as grout; however, the success of creating a tight seal in this way has not been fully established.

Membrane and *synthetic sheet curtains* can be used in applications similar to those of grout curtains and sheet piling. With this method, the membrane is placed in a trench surrounding or upgradient of the plume, thereby enclosing the contaminated source or diverting ground-water flow around the source. Placing a membrane liner in a slurry trench application has also been tried on a limited basis. Attaching the membrane to the impervious layer and forming perfect seals between the sheets is difficult, but necessary in order for membranes and other synthetic sheet curtains to be effective.

14.3.4 Interceptor Systems

Two types of interceptor systems used for source control are the *passive system*, which relies on gravity flow, and the *active system*, which uses pumps. An interceptor system consists of trenches excavated to a depth below the water table with a perforated collection pipe in the bottom. Active interceptor systems have vertical removal wells spaced along the interceptor trench or a horizontal removal pipe in the bottom of the trench. Active systems are usually backfilled with a coarse sand or gravel to maintain the stability of the wall. These interceptor systems can be used as preventive measures or in product recovery from ground water. Interceptor drains are generally used to either lower the water table beneath a contamination source or collect ground water from an upgradient source to prevent leachate from reaching uncontaminated wells or surface water. Interceptor systems are relatively inexpensive to install and operate; they are not, however, well suited for soils having a low permeability.

14.3.5 Hydrodynamic Controls

Hydrodynamic controls are used to isolate a plume of contamination from the normal ground-water flow regime to prevent the plume from moving into a well field, another aquifer, or the surface water. Hydrodynamic control is achieved through the use of well systems, including well point systems, deep-well systems, and pressure ridge systems.

A *well point system* consists of several closely spaced shallow wells connected to a main header pipe, which is then connected to a suction lift pump. Well point systems are used only for shallow

aquifers and are designed so that the system drawdown completely intercepts the plume of contamination.

Deep wells are similar to well point systems except they are used at greater depths and are normally pumped individually. These wells are used in consolidated formations where the water table is too deep for the economical use of a suction lift system.

Pressure ridge systems are produced by injecting uncontaminated water into the subsurface through a line of injection wells located upgradient or downgradient of a contamination plume. Upgradient ridges or mounds are used to force upgradient uncontaminated ground water to flow around a contaminant plume. The contaminated ground water is then collected by a line of downgradient pumping wells. The velocity of clean ground water into the plume is increased, thereby increasing flow to the recovery wells, which serves to wash the aquifer. Downgradient pressure ridge systems are normally used in combination with upgradient pumping wells that supply uncontaminated injection water. The injection of clean water produces a mound in the original water table that acts as a barrier by forming a ridge that contains the contaminated plumes and forces flow away from the mound.

A thorough knowledge of the hydrogeological conditions of the site is required for the development of a hydrodynamic control system. The effect of the injection wells on the drawdown and the radius of influence of the pumping wells must be analyzed. Monitoring of the system is necessary to ensure that ground water outside of the system is not being contaminated.

14.4 GROUND-WATER COLLECTION

The cleanup of a contaminated ground-water site involves the collection and treatment of the contaminated water. Some of the techniques used for source control are often used as part of a ground-water cleanup program, including interceptor systems, pumping well systems, and some of the techniques used for runoff alteration. In addition, *in situ* treatment, enhanced desorption, encapsulation, and biodegradation may be part of a ground-water cleanup plan.

A ground-water pumping system combined with a treatment system, also called a *pump-and-treat* system, is often designed for a specific ground-water contamination problem. [Figure 14.2](#) illustrates cross-sectional and plan views of a pump-and-treat system for an aquifer contaminated by an underground storage tank. Ground-water treatment systems are also used in conjunction with pumping systems designed to lower the water table or to contain a contaminant plume. The use of pump-and-treat systems is probably more widespread than that of all other restoration techniques combined. Large expenditures are made each year to prepare for and operate pump-and-treat remediation of ground-water contamination (Keely, 1989/T14.9). The hydrology of the site, the source of the contaminant, and the characteristics of the contaminant must be understood if an efficient and cost-effective pump-and-treat program is to be conducted.

When a significant amount of free product of a nonaqueous phase liquid (NAPL) is present in an aquifer, pump-and-treat systems are designed to maximize recover of the free product. Physical recovery techniques to remove free product include (1) a single-pump system producing a mixture of hydrocarbon and water that must be separated, but requiring minimal equipment and drilling; (2) a two-pump, two-well system utilizing one pump to produce a water table gradient and a second well to recover floating product; or (3) a single well with two pumps in which a lower pump produces a gradient and an upper pump collects free product. [Figure 14.3](#) illustrates a single-well, two-pump system for recovering LNAPLs. An aboveground oil–water separator generally is used to recover product for future use. Vacuum extraction of volatilizing contaminants also may be used to recover floating free product from a perched water table (Section 13.2).

Caution should be exercised during product recovery of LNAPL when an extraction well is used to control local gradients and collect free product in a cone of depression. Due to capillary forces

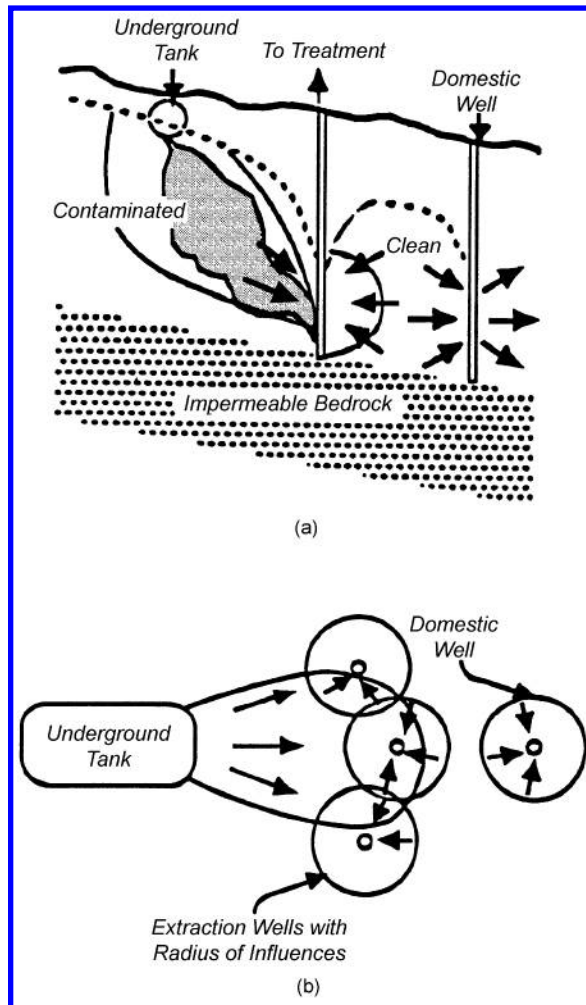


Figure 14.2 Pump-and-treat system: (a) cross-sectional view; (b) plan view (U.S. EPA, 1985).

in the subsurface aquifer material, trapped residual will constitute a continuous source of contamination to ground water that will persist after product removal from the water table is completed.

14.4.1 Well Field Pumping

The operation of a well field to remove ground water causes the formation of *stagnation zones* downgradient from the extraction wells, which must be considered in the design of a system. For example, if remedial action wells are located within the bounds of a contaminant plume, the portion of the plume lying within the stagnation zones will not be effectively remediated because the contaminants are removed from only the zone of advective ground-water flow. In this case, the only remediation in the stagnation zone will result from the process of chemical diffusion, which is very slow. Proper location of wells based on pumping rates and drawdown mitigates this effect to the extent possible.

The *tailing effect* can affect the removal and renovation of a ground water containing a low-solubility contaminant. Tailing is the slow, nearly asymptotic decrease in contaminant concentration in ground water moving through a contaminated geologic material. The contaminants migrate into

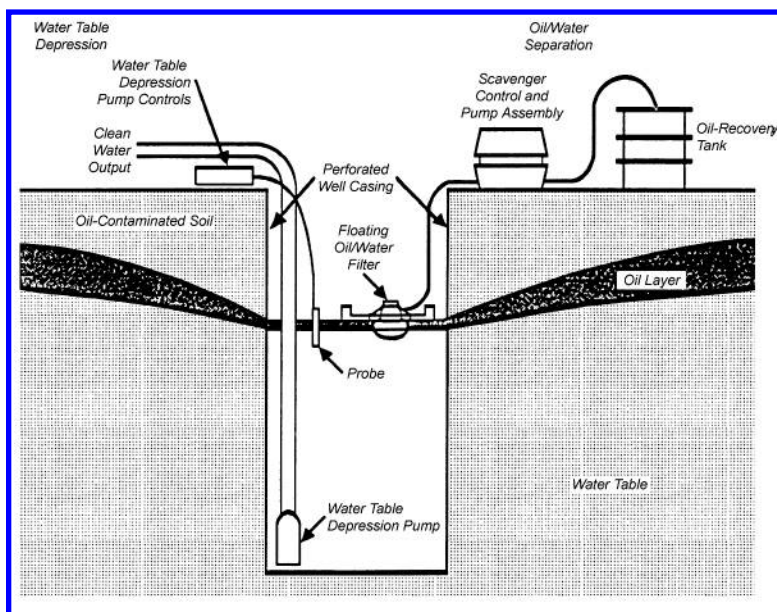


Figure 14.3 Product recovery using a water table depression pump and a floating oil/water filter (Sims and Sims, 1991c, after Nyer, 1985).

the finer pore structures of the geologic material and are slowly exchanged with the bulk water present in larger pores that is mobilized during pumping, thus resulting in “tailing” (Figure 14.4).

Many man-made and natural organic compounds found in ground water tend to adsorb to the organic and mineral components of the aquifer material. When water is removed by pumping, the contamination can remain on the aquifer material. The amount of remaining contaminant depends on the geologic materials and characteristics of the contaminants. Once sorbed to the geologic material, contaminants may desorb slowly into the ground water, thus requiring extended periods of pumping and treating to attain desired levels of restoration.

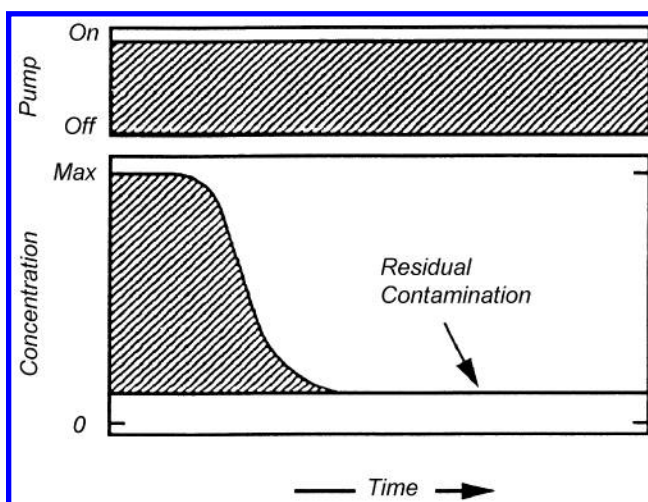


Figure 14.4 Stabilization of aquifer contaminant concentration during pump-and-treat resulting from tailing effect (Keely, 1989).

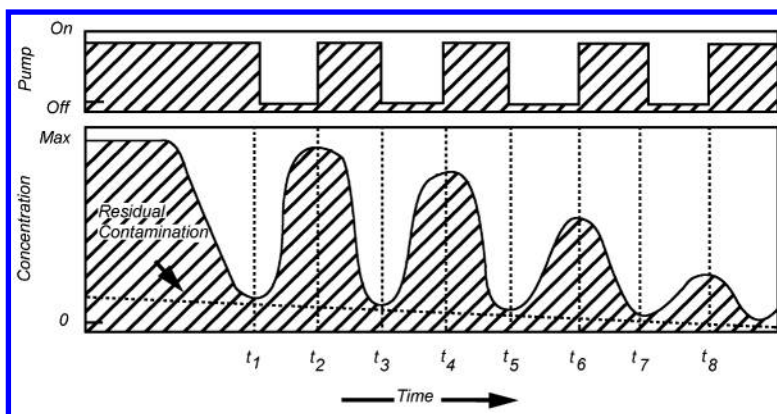


Figure 14.5 Pulsed pumping removal of residual contaminants reduces volume of water pumped and increases contaminant concentration in pumped water (Keely, 1989).

The removal of a water-insoluble liquid, such as gasoline, can be difficult since it may become trapped in the pore spaces of the soils and is not easily removed by pumping. Pumping ground water to remove the components of a residual phase initially may reduce the concentration, but this reduction may only be the result of dilution or lowering of the water table below the surface of contamination. A contaminant will not be removed faster than it is released into the ground water, so if the pumping stops for a period of time, water-soluble residual phase components will dissolve into the ground water, bringing the concentrations back up to their previous levels.

An innovation in pump-and-treat technology is *pulsed pumping*. This technique involves alternating the periods of pumping, allowing contaminants time to come to equilibrium with the ground water in each cycle (Figure 14.5). Equilibrium is achieved by diffusion from stagnant zones or zones of lower permeability, and by partitioning of sorbed contaminants or those associated with residual contaminant phases. Alternating pumping among wells in an extraction field can also establish active flow paths in the stagnant zones.

Another innovation is the use of pump-and-treat systems in conjunction with other remediation technologies. Examples are the use of extraction wells with barrier walls to limit plume expansion while reducing the amount of clean water pumped, and the use of surface ponds or flooding to flush contaminants from the vadose zone prior to collection by a pumping system.

14.4.2 Interceptor Systems

Interceptor systems (also discussed in [Section 14.3.4](#)) may be an alternative to well field pumping systems. The subsurface drains used in interceptor systems essentially function as an infinite line of extraction wells, and can perform many of the same functions as the wells. Subsurface drains create a continuous zone of influence in which ground water flows toward the drain (Wagner et al., 1986a/T12.7). Subsurface drains are installed perpendicular to the direction of ground-water flow and collect ground water from an upgradient source for treatment. Interceptor systems prevent leachate or contaminated ground water from moving downgradient toward wells or surface water.

Subsurface drains also have been used for recovery of DNAPLs (Figure 14.6a). When only the oil recovery drainline (ORD) is used (Figure 14.6b), water truncates the flow of product (DNAPL) due to the poor relative permeability of the product, as described previously, in the discussion of soil flushing. The water table depression drainline (WTDD) is an efficient method (see Figure 14.6c) to drag an oily product across the subsurface by viscous forces and thereby create a hydraulic head of oil above the ORD; however, oil also enters the WTDD, creating the need for aboveground separation of product and water. When both ORD and WTDD are used (Figure 14.6d), subsurface

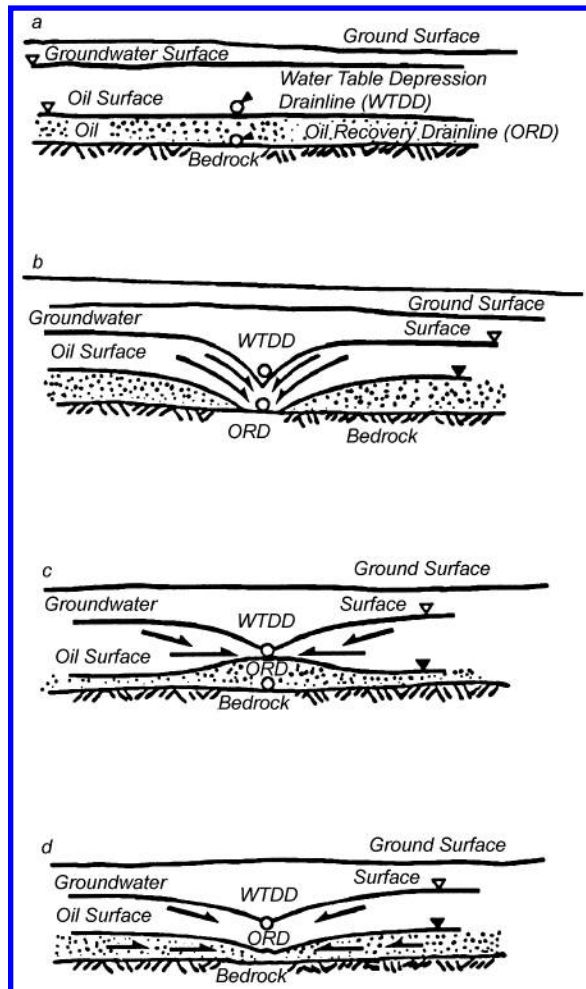


Figure 14.6 Use of drains to separate DNAPL from water where DNAPL rests on shallow bedrock; see text for explanation (Sims and Sims, 1991c, after Sale and Piontek, 1989).

separation of oil and water is achieved, minimizing aboveground separation requirements. This system (Figure 14.6d) is also efficient, since the permeability of oil is greatest in the oily contaminated subsurface, and the underground separation maintains water flowing in the water compartment and oil flowing in the oily compartment.

In stratified soils with variable hydraulic conductivities, the drain is normally installed on a layer with a low hydraulic conductivity to minimize leachate leakage under the drain and contamination flowing downgradient. An impermeable liner placed in the bottom of a trench can also be used to control underflow. The design, spacing, and location of drains for various soil and groundwater conditions are described further in Wagner et al. (1986a/T12.7).

The difficulty in installing subsurface drains at great depths generally limits the use of interceptor systems to shallow aquifers. Active interceptor systems use pumps to bring the ground water to the surface, but may have an advantage over well fields because fewer pumps are required. Use of passive systems using gravity flow may be possible where the topography allows placement of the surface treatment facility below the outlet of the subsurface drain. Interceptor systems may be preferred over well field pumping in cases where ground water must be removed over a period of several years, since the operation and maintenance costs are lower than for a well system.

Table 14.3 Process Applicability Matrix for Hazardous Waste Leachate Treatment Methods (McArdle et al., 1987)

Technology	Suspended Solids	Oil, Grease, Immiscible Liquids	pH (acidic, basic)	Total Dissolved Solids	Metals	Cyanides	Volatile Organics	Semivolatile Organics	Pesticides, PCB's	Pathogens
Sedimentation	+	+	o	o	o	o	o	o	o	o
Granular-media filtration	+	–	o	o	o	o	o	o	o	o
Oil/water separation	o	+	o	o	o	o	o	o	o	o
Neutralization	o	o	+	o	o	o	o	o	o	o
Precipitation/flocculation sedimentation	+	+	o	+	+	o	o	o	o	o
Oxidation/reduction	–	–	o	o	+	+	o	+	+	+
Carbon adsorption	–	–	o	o	+	+	+	+	+	+
Air stripping	–	–	o	o	o	o	+	o	o	o
Steam stripping	–	–	–	o	o	o	+	o	o	o
Reverse osmosis	–	–	–	+	+	+	o	o	+	+
Ultrafiltration	–	–	–	+	+	o	o	+	+	+
Ion exchange	–	–	o	+	+	+	o	o	–	o
Wet-air oxidation	o	o	o	o	+	+	+	+	o	o
Activated sludge	–	–	–	–	o	–	+	+	o	o
Sequencing batch reactor	–	–	–	o	–	o	+	+	o	o
Powdered activated carbon treatment (PACT)	+	–	–	o	–	o	+	+	+	o
Rotating biological contactor	o	–	–	o	–	o	+	+	o	o
Trickling filter	–	–	–	o	–	o	+	+	o	o
Chlorination	o	–	–	o	o	+	o	o	o	+

Note: (+) process is applicable for removal of the contaminant; (o) process is not applicable for removal of the contaminant; (–) process is not applicable unless the leachate is pretreated for removal of the contaminant.

14.4.3 Ground-Water Treatment after Removal

Treatment technologies for pumped or intercepted ground water can be grouped into three broad areas: physical, chemical, and biological. *Physical* treatment methods (Section 14.5.1) include adsorption, density separation, filtration, reverse osmosis, air and steam stripping, and incineration. Precipitation, oxidation–reduction, ion exchange, and neutralization are commonly used *chemical* treatment methods (Section 14.5.2). *Biological* treatment methods (Section 14.5.3) include activated sludge, aerated surface impoundments, anaerobic digestion, trickling filters, and rotating biological discs. Table 14.3 identifies potential processes for treatment of hazardous waste leachate or contaminated ground water, and Table 14.4 summarizes treatment process capabilities for landfill leachate. Figure 14.7 identifies general suitability of different treatment methods for organic and inorganic contaminants. Moving from top to bottom in Figure 14.7, treatment methods are able to handle increasing concentrations of contaminants.

Table 14.4 Summary of Landfill Leachate Process Capabilities (Pohland and Harper, 1989)

	BOD ₅		COD		TKN		Fe		Zn		Ni		Comments
	Rem., %	Effl., mg/l	Rem., %	Effl., mg/l	Rem., %	Effl., mg/l	Rem., %	Effl., mg/l	Rem., %	Effl., mg/l	Rem., %	Effl., mg/l	
Aerobic Biological Processes													
Activated sludge	95	100	95	500	70–95	10–100	96–99	10–40	96–99	3–10	60	0.25	Θ _c = 6–10 days
Combined leachate and sewage	94–99	3–15	92–98	25–60	—	—	—	—	—	—	—	—	Ratio < 5%
Aerated lagoon	99	5–60	92–98	300–800	40–70*	40–80	99	0.2	—	—	—	—	Θ _c > 10 days
Stabilization pond	93–99	10–100	99	100–400	70–99	4–100	80–99	1–100	—	—	—	—	τ > 40 days
Aerobic fixed film*	93–99	10–100	99	100–400	70–99	4–100	80–99	1–100	—	—	—	—	τ > 40 days
Anaerobic Biological Processes													
Attached growth	85–98	100–900	75–95	200–1000	—	—	80–99	5–25	80–99	0.5–10	10–80	0.1–1	Θ _c > 10 days
Suspended growth	85–98	100–900	75–95	200–1000	—	—	80–99	5–25	80–99	0.5–10	10–80	0.1–1	Θ _c > 5 days
Leachate recycle	NA	<100	NA	<5	NA	20–1000	NA	5–50	NA	0.2–1	NA	—	Θ _c > 500 days
Physical/Chemical Processes													
Coagulation	—	—	12	100–10,000	—	—	95–99	2–17	75–98	<1	—	—	Lime, alum, ferric chloride
Oxidation	—	—	10–50				99	<1	90	<1	—	—	Ozone, chloride permanganate
Reverse Osmosis	—	—	60–90** 86–94	1000–8000 <10	—	—	—	—	—	—	—	—	Raw leachate Pretreated leachate
Ion exchange	—	—	40–70	100–300	—	—	40–80	1–10	20–96	<1	14–96	<1	Commercial IX resins and GG
Adsorption	—	—	75–99	<10	—	—	65–95	2–15	—	—	—	—	GAC and PAC

Note: Rem. = Removal; Effl. = effluent.

* Insufficient data to make an adequate judgment.

**TOC basis.

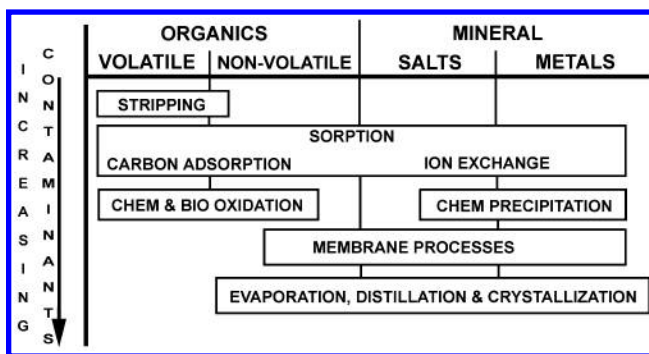


Figure 14.7 Contaminated ground water treatment matrix (U.S. EPA, 1990).

14.5 GROUND-WATER PUMP-AND-TREAT METHODS

14.5.1 Physical Treatment

Table 14.5 summarizes the advantages and disadvantages of seven methods for physically treating contaminated ground water.

Adsorption. *Granular activated carbon* (GAC) is the most widely used material for adsorption of organic contaminants from water. *Synthetic resins* are also used as adsorbents, but they are expensive and their use is currently in the developmental stages. Synthetic resins trap contaminants within the chemical structure of the resin, whereas GAC traps contaminants within the physical pore structure of the carbon. The extent of adsorption depends on the strength of the molecular attraction among the adsorbent and the adsorbate, the molecular weight of the contaminants, the type and characteristic of the adsorbent, the electrokinetic charge, the pH, and the surface area (Rich and Cherry, 1987).

A typical adsorption system consists of a large vessel filled with adsorbent with an inlet zone for contaminated water and an outlet zone for treated water. Influent water contacts the adsorbent for a specified period and then exits for collection, disposal, recharge, or further treatment. GAC systems are often arranged with several units in parallel or in series to allow for the most efficient treatment possible. Once the micropore surfaces are saturated, little or no further adsorption occurs. Some contaminants may be released during treatment, resulting in a gradual increase in the effluent contaminant concentration. When the concentration exceeds the desired limit, the adsorbent must be replaced and the used adsorbent discarded or regenerated.

Adsorption using GAC is an effective and reliable technique for removing low-solubility organics and some metals and inorganic species. It can be used for treating a wide range of contaminants over a broad concentration range and is not adversely affected by toxics. Carbon adsorption is often used after preliminary treatment steps to reduce high organic and suspended solids loads to improve the efficiency and extend the life of the GAC or synthetic resin.

Density Separation. Ground water with high concentrations of settleable or floatable organics or excess suspended solids may be treated by density separation. *Clarifiers* separate liquids of differing density. Suspended solids can be removed by *settling chambers* or *sedimentation basins*. Sometimes clay-size suspended solids are treated with *flocculents* that cause the small particles to aggregate, thus speeding the rate at which they settle.

Filtration. Filtration is a reliable and effective means of removing suspended solids provided the solids concentration is not excessive. In filtration, suspended solids are removed from ground water by forcing the fluid through a porous medium. Filtration systems use a variety of media. Typical high-rate gravity or pressure filters consist of a bed of granular particles (usually sand or

Table 14.5 Advantages and Disadvantages of Physical Methods of Ground Water Treatment

Method	Advantages	Disadvantages
Absorption	<ul style="list-style-type: none">• GAC is effective and reliable for removing low-solubility organics• GAC can be used for treating a wide range of contaminants over a broad range of concentrations• GAC is not adversely affected by toxics	<ul style="list-style-type: none">• High operation and maintenance costs• GAC is intolerant of high suspended solids• Pretreatment is required for oil and grease greater than 10 mg/l• Synthetic resins are intolerant of strong oxidizing agents and suspended solids
Density separation	<ul style="list-style-type: none">• Minimal operational requirements• Readily available equipment may be used	<ul style="list-style-type: none">• Incomplete removal of hazardous compounds• Sludge generated requires disposal
Filtration	<ul style="list-style-type: none">• Reliable and effective means of removing low levels of solids• Equipment is readily available and is easy to operate and control	<ul style="list-style-type: none">• Filters clog if suspended solids concentration is high• Backwash water requires further treatment
Reverse osmosis	<ul style="list-style-type: none">• Ability to reduce both inorganic and organic dissolved solids	<ul style="list-style-type: none">• Units are subject to chemical attack, fouling, and plugging• Pretreatment requirements may be extensive
Stripping (packed tower)	<ul style="list-style-type: none">• Equipment is relatively simple and startup and shutdown can be accomplished quickly• Modular design is suited for hazardous waste applications	<ul style="list-style-type: none">• Sensitive to pH, temperature, and fluxes in hydraulic load• May be cost prohibitive at temperatures below freezing• Often only partially effective and must be followed by another process• May cause air pollution problems
Incineration	<ul style="list-style-type: none">• Can be used to destroy contaminants in liquid, gaseous, and solid waste	<ul style="list-style-type: none">• Thickening and dewatering may be required prior to incineration• May pose air pollution problems• Produces an inorganic ash that may be hazardous• May require costly fuel or power for operation
Wet-air oxidation	<ul style="list-style-type: none">• Effective on concentrated wastes that are not readily biodegradable• Generates no air pollution	<ul style="list-style-type: none">• Energy intensive

Source: Compiled from U.S. EPA (1985), Knox et al. (1984), Nielsen (1983), and Wagner et al. (1986).

sand with anthracite coal). The bed is supported by an underdrain system that allows the filtered liquid to be drawn off.

Filtration is often preceded by chemical coagulation and sedimentation or biological treatment, and often precedes activated carbon units to decrease the suspended solids load. The filter must be backwashed at appropriate intervals; the backwash water then requires further treatment.

Reverse Osmosis. Osmosis is the spontaneous flow of a water molecule from a dilute solution, through a semipermeable membrane, to a more concentrated solution by osmotic pressure (see Section 2.4.1). If enough pressure is placed on the concentrated solution to overcome osmotic pressure, the water will flow toward the dilute phase in a process known as reverse osmosis. A reverse osmosis unit is composed of a membrane, a membrane support structure, a containing vessel, and a high-pressure pump. Reverse osmosis allows the concentration of contaminants to build up in a circulating system on one side of the membrane, while relatively pure water passes through the membrane and is discharged. The resulting concentrated solution containing the contaminants and salts requires subsequent special handling.

Reverse osmosis separates ions and small molecules in true solution from water, producing a product low in dissolved solids concentration, both organic and inorganic. This method is used primarily for cleaning low-flow waste streams containing highly toxic contaminants. Good removal can be expected for high-molecular-weight organics and charged univalent ions. However, mem-

brane technology has been developed to the extent that low-molecular-weight organics such as alcohols, ketones, amines, and aldehydes can also be removed. Reverse osmosis has been demonstrated to be an effective treatment technology, although wastes containing high concentrations of various organics may not be treatable with this method due to excessive membrane dissolution or fouling. Pretreatment such as suspended solids removal, pH adjustment, and removal of oxidizers and oil and grease is also required.

Stripping. Stripping is a mass transfer process in which volatile contaminants are removed from the aqueous phase and transferred to the gaseous phase. This process is accomplished by passing air or steam through the liquid wastes. Air stripping has been applied to ground water for removal of VOCs, including trichloroethylene, trihalomethane, chlorobenzene, and vinyl chloride. Biological treatment or carbon adsorption may follow air stripping to remove nonstrippable organics or as a final polishing step.

Air stripping systems include packed tower, cross-flow cooling type tower, coke tray aerator, or stripping lagoons with diffused air. The *packed tower* system works on the principle of countercurrent flow. In this method, the water stream flows down through the packing, while the air flows upward and is exhausted through the top to the atmosphere or to emission control devices (e.g., condensers, carbon adsorption filters). In the *cross-flow tower* method, water flows down through the packing as with the countercurrent packed tower; however, in this method the air is pulled across the water flow path by a fan. The *coke tray aerator* is a simple, low-maintenance process that requires no blower. The water being treated trickles through several layers of trays, producing a large surface area for gas transfer and induced draft stripping. *Diffused aeration* stripping uses aeration basins or lagoons similar to those used in wastewater treatment. Water flows through the basin, and the air is dispersed through diffusers at the bottom of the basin. Since the air-to-water ratio is significantly lower in the basins than in either the packed or cross-flow towers, efficiency is typically lower.

Temperature affects the mass transfer coefficient of a compound. This is important when considering stripping for contaminated ground water that contains very soluble compounds (i.e., low Henry's law constants). High water solubility makes their efficient removal to low levels by ambient-temperature air stripping almost impossible. Removal efficiency increases dramatically with increasing temperature and less sharply with the air-to-water ratio. High temperature air stripping or steam stripping offers increased flexibility in such cases.

Incineration. Incineration offers one of the most effective technological methods for complete destruction of organic compounds. It would not, however, normally be applied directly to pumped ground water. Instead, ground water containing high concentrations of miscible organics or organic phases removed from ground water would be a potential candidate for incineration. Incineration uses heat under controlled conditions to decompose a substance into products that generally include CO_2 , H_2O vapor, SO_2 , NO_x , HCl , and products of incomplete combustion. Temperature control of the burning and air pollution control equipment are typically required to prevent the release of undesirable combustion products into the atmosphere. Incineration methods can be used to destroy organic contaminants in liquid, gaseous, and solid wastes.

The most common incineration technologies are liquid injection, rotary kiln, fluidized bed, and multiple hearth. *Rotary kiln* and *multiple hearth* incinerators can be used with most organic wastes, including solids, sludges, liquids, and gases. *Liquid injection* incinerators are limited to pumpable slurries and liquids. *Fluidized-bed* incinerators work well for organic liquids, gases, and granular or well-processed solids. Other methods for the thermal destruction of wastes are under development. These methods include molten salt, plasma arc torch, circulating bed, high temperature fluid wall, pyrolysis, supercritical water, advanced electric reactor, and vertical tube reactor. These advanced incineration technologies are briefly described in Wagner et al. (1986).

Wet-Air Oxidation. Wet-air oxidation is a process in which dissolved or suspended organic substances in the aqueous phase are oxidized at high temperatures and pressures. The extent of oxidation is a function of the nature of the organics and the temperature and detention time in the

reactor. As with incineration, its most likely use would be to treat residual liquids with high concentrations of organic and oxidizable inorganic components resulting from treating contaminated ground water. Wet-air oxidation is particularly applicable to concentrated streams containing pesticides, herbicides, or other complex organics that are not readily biodegradable (Rich and Cherry, 1987/T12.7).

14.5.2 Chemical Treatment

Table 14.6 summarizes the advantages and disadvantages of five methods for chemically treating contaminated ground water.

Neutralization is a process in which an acid or base is added for pH adjustment. It is a relatively simple unit process that can be performed using ordinary and commonly available treatment equipment. It is often used prior to other treatment processes such as biological treatment, carbon adsorption, ion exchange, air stripping, or chemical oxidation–reduction processes where the pH of the liquid to be treated is critical.

Chemical precipitation is a physicochemical process whereby a substance in solution is transformed to the solid phase. Precipitation results from the addition of a chemical that will react with the contaminant in solution to form an insoluble compound. Changes in temperature may also reduce contaminant solubility and result in precipitation. The most common application of precipitation in contaminated ground-water treatment is the addition of chemicals to remove metals such as carbonates, hydroxides, or sulfides. Many precipitation reactions (e.g., metal sulfides) do not readily form settleable floc but precipitate as very fine and relatively stable colloidal particles. When this occurs, flocculating agents (e.g., metal salts or polyelectrolytes) are added to cause flocculation of the metal sulfide precipitates. The effectiveness of precipitation/flocculation reactions depends upon the nature and concentration of the contaminants and upon the process design. The process design must consider the optimum chemicals and dosages, suitable chemical addition systems, optimum pH and mixing requirements, temperature, sludge production, and dewatering characteristics.

Oxidation–reduction reactions raise (oxidation) or lower (reduction) the oxidation state of a substance or substances in order to reduce toxicity or solubility, or to transform the substance to a form that can be handled more easily. Commonly used reducing agents include sulfite salts, sulfur

Table 14.6 Advantages and Disadvantages of Chemical Methods of Ground Water Treatment

Method	Advantages	Disadvantages
Neutralization	<ul style="list-style-type: none"> • Uses commonly available equipment 	<ul style="list-style-type: none"> • Potential for air emissions of acid fumes • Some neutralization agents are corrosive
Precipitation	<ul style="list-style-type: none"> • Useful for most hazardous waste streams 	<ul style="list-style-type: none"> • Limited by the presence of complexing agents in the waste • Precipitate may be a hazardous waste
Oxidation treatment	<ul style="list-style-type: none"> • Uses simple, readily available equipment 	<ul style="list-style-type: none"> • Costs are generally higher than biological • Some organics are resistant to most oxidants • Partial oxidation may generate toxic compounds • Oxidizing chemicals are potentially hazardous
Reduction	<ul style="list-style-type: none"> • Uses simple, readily available equipment and reagents 	<ul style="list-style-type: none"> • No current applications for reducing organic compounds
Ion exchange	<ul style="list-style-type: none"> • Removes a broad range of ionic species • Columns available commercially • Units are compact and not energy intensive 	<ul style="list-style-type: none"> • Must monitor effluent to monitor resin performance • Effectiveness reduced by high suspended solids and certain organics • Regeneration solution must be disposed

Source: Compiled from U.S. EPA (1985), Knox et al. (1984), Nielsen (1983), and Wagner et al. (1986).

dioxide, and the base metals (i.e., iron, aluminum, and zinc). Chemical *reduction* is used primarily to reduce hexavalent chromium, mercury, and lead. Currently, no practical applications involve reduction of organic compounds. *Oxidation*, however, is used extensively in the treatment of organic wastes. Oxidizers most often used in wastewater treatment include oxygen or air, ozone, ozone with ultraviolet light, chlorine gas, hypochlorites, chlorine dioxide, and hydrogen peroxide.

Ion exchange resins remove toxic ions from the aqueous phase through exchange with relatively harmless ions held by the ion exchange material. Ion exchange systems function well for relatively dilute solutions of variable composition. Ion exchange is used to remove a broad range of ionic species from water, including anionic or cationic soluble metallic elements, inorganic anions, organic acids if at an alkaline pH, and organic amines when solution acidity is favorable for the formation of the acid salt (DeRenzo, 1978/T12.7).

The ion exchange effluent is monitored to determine when ion exchange resin bed exhaustion has occurred. The regenerant produced can be an appreciable percentage of the treated flow and will require subsequent disposal or treatment. This aspect of ion exchange can often reduce the cost-effectiveness of this technology, particularly if waste concentrations are high.

14.5.3 Biological Treatment

Table 14.7 summarizes the advantages and disadvantages of four methods for biologically treating contaminated ground water.

Activated Sludge. Activated sludge is a suspended growth biological treatment system in which a contaminated solution is mixed in an aeration basin with an active microbial population. The bacteria present are capable of biologically degrading the organic contaminants to cellular material,

Table 14.7 Advantages and Disadvantages of Biological Methods of Ground Water Treatment

Method	Advantages	Disadvantages
Activated sludge	<ul style="list-style-type: none"> Effective for readily treated organics Process reliable in absence of shock loads Technology is highly developed Can tolerate higher organic loads than most biological treatment processes High degree of flexibility 	<ul style="list-style-type: none"> High capital costs Generates sludge that may be high in metals and refractory organics Sensitive to heavy metals, toxic organics at high concentrations, and suspended solids Fairly energy intensive
Surface impoundments	<ul style="list-style-type: none"> Well demonstrated for stabilization of organics Require minimal energy 	<ul style="list-style-type: none"> Sensitive to shock loadings and temperature Anaerobic lagoons may generate gas Must be timed to prevent seepage into ground water
Trickling filter	<ul style="list-style-type: none"> Not highly sensitive to shock loads Suitable for removal of suspended or colloidal matter Can be used as a roughing filter to even out organic loads 	<ul style="list-style-type: none"> Potential for odor problems Generates sludge that may be high in refractory organics and sorbed metals Sensitive to metals and oil and grease Can handle only very low organic loads compared to activated sludge Vulnerable to below-freezing temperatures
Rotating biological discs	<ul style="list-style-type: none"> Can handle larger flow variations and higher organic shock loads than activated sludge Modular construction provides flexibility to meet increased or decreased treatment needs 	<ul style="list-style-type: none"> Potential for odor problems Vulnerable to climate changes if not covered Supplemental aeration may be required Can handle only relatively low-strength wastes compared to activated sludge Excess biological growth of undesirable microorganisms under certain conditions

Source: Compiled from U.S. EPA (1985), Knox et al. (1984), Nielsen (1983), and Wagner et al. (1986).

carbon dioxide, and water. Following the aeration step, the organic matter is removed, the microorganisms are separated from the liquid by gravity settling in clarifiers, and a portion of the settled microorganisms are recycled to the aeration basin. The new cells developed as a result of cell synthesis are removed from the system for further treatment and disposal.

Various modifications of the conventional activated sludge process include pure oxygen aeration, oxygen-enriched aeration, extended aeration, step feed, and contact stabilization. The contaminants present in the liquid to be treated, site considerations, costs, and required effluent limits all influence the type of activated sludge system selected.

Activated sludge has not been used as extensively for ground-water treatment as have activated carbon, filtration, and precipitation followed by flocculation; however, the process is well established for treating a wide variety of organic contaminants (U.S. EPA, 1985/T12.7). Limiting factors in the use of activated sludge for contaminated ground-water treatment include its inability to treat low concentrations of contaminants, the relatively long time required for organism acclimation, the long detention times required for some complex contaminant degradation, the sensitivity of the system to shock loads, and the potential for the sludge produced to be hazardous.

Surface Impoundments. Surface impoundments are large shallow ponds or lagoons with suspended microbial populations in much lower concentrations than in activated sludge systems. Detention times on the order of weeks are typical, and natural or applied aeration maintains aerobic conditions. Surface impoundments require large land areas, and because low temperatures adversely affect performance, they are not suitable for climates where the temperature remains below freezing for appreciable lengths of time. Advantages are low operating costs and minimal energy use compared to other biological treatment methods.

Anaerobic lagoons or *anaerobic digesters*, which are totally enclosed, may be used for organic contaminant degradation. The anaerobic digestion process is relatively easy to operate, produces a minimum of sludge, and is energy efficient. Digesters are often maintained at elevated temperatures to increase microbial activity and the degradation rate. These systems have applications to high-strength contaminated water and to residuals such as sludges.

Trickling Filters. A trickling filter system is a fixed-film biological treatment process in which contaminated water is brought into contact with microorganisms attached to solid media. The organisms in the slime layer coating the media metabolize the organics in the water, producing biological mass, carbon dioxide, and water. Air moving countercurrent to the waste flow through the filter provides oxygen to the microorganisms.

The *biological tower* is a modification of the trickling filter process in which plastic or wood is stacked in a column that typically reaches 16 to 20 ft in height. The contaminated water is sprayed across the top of the tower, and as this water moves downward, air is pulled upward. A slime layer of microorganisms develops on the media and removes the organic contaminants as the water trickles over it. High-void-ratio plastic media are used to reduce bed plugging and to improve treatment efficiency.

Trickling filters are more resistant to high organic shock loads and cost less to operate than activated sludge systems. The initial capital cost is higher, however, and final effluent concentrations are typically higher as well.

Rotating Biological Discs. A rotating biological disc system is a fixed-film biological treatment process consisting of a series of mechanically rotated discs connected by a shaft and set in a basin or trough. Approximately 40% of each disc's surface area is submerged in the basin, and as the contaminated water passes through the basin, the microorganisms growing on the disc metabolize the organics in the water. As the discs rotate, the microorganisms come in contact with the air from which they obtain oxygen for growth. Rotating biological discs are compact, can handle large flow fluctuations and high organic shock loads, and do not require an aeration system. These systems, however, are subject to problems resulting from continuous excess loading such as excess biological film thickening and snail infestations.

14.6 *IN SITU* TREATMENT

In situ treatment is an alternative to the removal and subsequent treatment of contaminated ground water. This method requires minimal surface facilities and minimizes exposure to the contaminant. The success of various treatment methods is highly dependent on physical factors, including aquifer permeability, the characteristics of the contaminants involved, and the geochemistry of the aquifer material.

In situ treatment technology has not yet been developed to the extent of other currently available technologies for restoring contaminated aquifers. However, some *in situ* treatment technologies have demonstrated success in actual site remediations (Wagner et al., 1986a/T12.7). Laboratory and pilot-scale testing generally must be performed to evaluate the applicability of a particular technology to a specific site.

In situ treatment technologies may be grouped into two broad categories: physical/chemical and biological. Brief descriptions follow of the available technologies that have potential for success at hazardous waste sites.

14.6.1 *In Situ* Physical/Chemical Treatment

Organic and inorganic contaminants may be treated chemically to cause immobilization, mobilization for extraction, or detoxification. The application of *oxidation* and *reduction* reactions to *in situ* treatment is largely conceptual, but potentially may be used to accomplish immobilization by precipitation, mobilization by solubilizing metals or organics, or detoxification of metals and organics (Wagner et al., 1986a/T12.7). The chemicals, however, have the potential to degrade compounds other than the one targeted and to form degradation products that may be more toxic than the one removed.

Precipitation, chelation, and polymerization technologies are used to immobilize contaminants. Mobilization of contaminants is accomplished by soil flushing or vacuum extraction. Neutralization, hydrolysis, and permeable treatment bed technologies may be used for detoxification. *In situ* physical/chemical treatment processes generally require the installation of a series of injection wells at the head of or within the plume of contaminated ground water.

Immobilization. *Precipitation, chelation, and polymerization* are three methods used to immobilize a contaminant to prevent its migration out of the contaminated area. Precipitation using caustic solutions is effective in immobilizing dissolved metals in ground water. Chelation may also be effective in immobilizing metals, although considerable research is needed (Wagner et al., 1986a/T12.7). Polymerization is effective in immobilizing organic monomers. However, the chemicals added to the contaminants in the ground water may react to form toxic by-products. Precipitation and polymerization will lower the hydraulic conductivities near the injection wells, making closely spaced wells necessary for effective treatment. Solidification methods used for treatment of soils can also immobilize contaminants.

Mobilization for Extraction. *Soil flushing* is the process of flooding a contaminated area with water or a solvent to mobilize the contaminant, followed by the collection of the elutriate. This technique is used in combination with previously discussed collection and treatment technologies. The process is based on the solvent solubilizing or chemically reacting with the contaminants and mobilizing them into the solvent phase. Water is used if the contaminant is readily soluble. Acid solutions tend to flush metals and basic organics. Three possible methods for flushing hydrocarbons from soil include *thermal* or *steam flooding* for shallow depths, and *alcohol flooding* on a larger scale. Mobilization of contaminants may also be accomplished by injecting surfactants into the aquifer matrix.

Vacuum extraction, or in situ volatilization, is used to extract volatile organic contaminants from the vadose zone. An extraction system may consist of a series of slotted PVC wells configured to span the area of contamination. Air inlet wells located inside and outside of a contaminated

ground-water plume increase the introduction of air from the atmosphere. Vacuum extraction is best suited for areas of high, relatively homogeneous permeability, with no underground structures. Caution must be exercised, however, because extracted vapors may be explosive.

Radio frequency (RF) heating has been under development since the mid-1970s, and the concept is being applied to *in situ* decontamination of uncontrolled hazardous waste landfills and sites (Rich and Cherry, 1987/T12.7). In this process, the ground is heated with radio frequency waves that vaporize the hazardous contaminants. The vapors emanating from the soil are then treated. Phelan (2000/T13.9) provides a modern review of RF heating technology as applied to the removal of organic contaminants from the subsurface, including discussion of field implementation, monitoring, limitations, and economics.

Detoxification. *Neutralization* of ground water may be accomplished by injecting dilute acids or bases into the aquifer through injection wells to adjust pH to the desired level (see Section 3.2.1). Tolman et al. (1978/T14.9) recommended that neutralization only be applied to ground water at industrial waste disposal sites since municipal landfills, which constantly generate anaerobic decomposition products, would require neutralization over a long period.

Hydrolysis may be used for detoxification (see Section 3.3.2); however, the intermediate products formed during hydrolysis of a particular compound must be known since they may be more toxic than the targeted compound. Esters, amides, carbamates, phosphoric and phosphonic acid esters, and pesticides are potentially degradable by hydrolysis (Wagner et al., 1986a/T12.7).

Permeable treatment beds are often used to remediate migrating leachate plumes. In this method, trenches are filled with a reactive permeable medium that reacts with the contaminated ground water to produce a nonhazardous soluble product or a solid precipitate. Limestone, activated carbon, and other ion exchange resins are frequently used in a trench in the aquifer. Permeable treatment beds are applicable in shallow aquifers since the trench must be constructed down to an impermeable layer. The period of effectiveness is limited by the loss of reactive capacity and by plugging with solids.

14.6.2 *In Situ* Biological Treatment

Biological treatment involves the use of microorganisms to break down hazardous organic compounds into nonhazardous materials. The site hydrology, environmental conditions, and biodegradability of the contaminants are factors that determine the potential effectiveness of *in situ* biological treatment. Most compounds are more rapidly degraded aerobically; however, some compounds will only degrade under anaerobic conditions (see Sections 3.5.3 and 3.5.4). Biodegradation in ground water and solids can be a slow process and may take several years for completion, depending on the compounds present. *In situ* biodegradation, however, is a desirable method of treatment because the contaminants are destroyed; thus, removal of ground water for external treatment and residual handling can possibly be avoided.

There are two basic approaches to *in situ* biodegradation. The first relies on the natural biological activity in the subsurface (Section 3.5). This approach usually involves minimal intervention other than use of containment measures (Section 14.3) to prevent further movement of contaminants. Since organic contaminants tend to create anaerobic conditions, contaminants that are degraded anaerobically are the most likely candidates for using the natural biological activity in an aquifer for treatment. The second approach, called *enhanced bioremediation*, involves the stimulation of the existing microorganisms by adding nutrients and oxygen to promote aerobic degradation of contaminants.

The majority of microbes in the subsurface are firmly attached to soil particles. Nutrients must be brought to the active sites by advection and diffusion of water in the saturated zone or by soil gas in the vadose zone. Most often the compounds to be degraded for microbial energy and cell synthesis are transported in the aqueous phase by infiltrating water, or by advective flow through the ground water. In the vadose zone, volatile organic compounds can move readily as vapors in the soil gas where oxygen is present. Below the water table, aerobic metabolism is limited by the

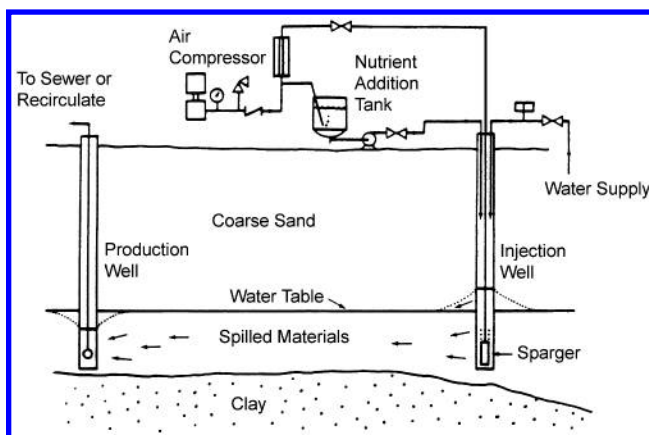


Figure 14.8 Typical schematic for aerobic subsurface bioremediation (Sufliya, 1989, after Lee et al., 1988).

low solubility of oxygen in water. Factors that control the rate of biological activity are the stoichiometry of the metabolic process, the concentration of the required nutrients in the mobile phases, the flow of the mobile phases, the opportunity for colonization in the subsurface by metabolically capable organisms, and the toxicity of the waste.

Much of the development work in the area of ground-water and soil remediation by biodegradation has been performed using petroleum products. The number of gasoline stations, underground tanks, and gasoline pipelines throughout the country and the potential for ground-water contamination have prompted considerable laboratory and field studies on *in situ* biodegradation of hydrocarbons. Figure 14.8 illustrates a typical system in which microbial nutrients are mixed with ground water and circulated through the contaminated portion of the aquifer through a series of injection and recovery wells. Oxygen is supplied by sparging air into the injection wells. The increased supply of nutrients and oxygen stimulates biodegradation of the hydrocarbons. Wells should be screened to accommodate seasonal fluctuations in the level of the water table. Some operational designs are closed loop, in which the water is recycled; thus, unused nutrients can be reinjected, disposal of potentially hazardous ground water is avoided, and the need for makeup water is reduced.

The first step in the process is to use physical methods to recover as much of the gasoline as possible. Then a detailed investigation of the hydrogeology is undertaken to determine the extent of the contamination. Laboratory studies are conducted to determine if the native microbes can degrade the contaminants and to determine the combination of minerals required to promote maximum cell growth at the ambient ground-water temperature and under aerobic conditions. Considerable variations in nutrient requirements among aquifers have been noted.

The field investigations and laboratory studies guide the design and installation of a system of wells for injecting the nutrients and oxygen and controlling subsurface flow. Controlling the ground-water flow is critical to moving oxygen and nutrients to the contaminated zone and optimizing the degradation process.

The technique described above does not provide for treatment above the water table. Soils contaminated by leaking underground storage tanks may be physically removed during the process of removing the tank; however, this may not be practical with deep water tables or large areas of contamination. An alternative to soil removal is the construction of one or more infiltration galleries (Figure 14.9). Infiltration galleries allow movement of the injection solution through the unsaturated zone and the saturated zone, resulting in potential treatment of source materials that may be trapped in the pore spaces of the unsaturated zone. Oxygen may be added to the infiltrated water during an in-line stripping process for volatile organic contaminants or through aeration devices placed in the infiltration galleries.

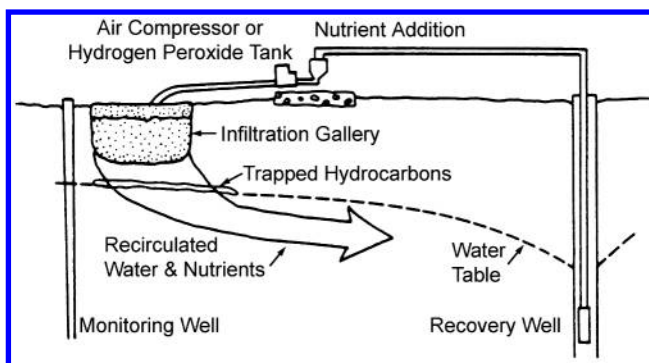


Figure 14.9 Use of infiltration gallery for recirculation of water and nutrients for *in situ* bioremediation (Sufliya, 1989, after Lee et al., 1988).

Table 14.8 Estimated Volumes of Water or Air Required to Renovate Subsurface Material Containing Hydrocarbons at Residual Concentrations

Texture	Proportion of Total Subsurface Occupied by:			Volumes Required to Meet Hydrocarbons Oxygen Demand	
	Hydrocarbons (when drained) ^a	Air (when drained) ^a	Water (when flooded) ^a	Air ^b	Water ^c
Stone to coarse gravel	0.005	0.4	0.4	250	5000
Gravel to coarse sand	0.008	0.3	0.4	530	8000
Coarse to medium sand	0.015	0.2	0.4	1500	15,000
Medium to fine sand	0.025	0.2	0.4	2500	25,000
Fine sand to silt	0.040	0.2	0.5	4000	32,000

^a Typical values taken from Clapp and Hornberger (1978); see Appendix F for reference.

^b Oxygen content assumed to be 200 mg/l and the hydrocarbons to be completely metabolized to carbon dioxide.

^c Water content assumed to be 10 mg/l and the hydrocarbons to be completely metabolized to carbon dioxide.

Source: Adapted from U.S. EPA (1987a).

The rate of bioreclamation of hydrocarbons is effectively the rate of supply of oxygen. Table 14.8 compares the number of times the water in the aquifer, or the air above it, must be replaced to restore subsurface materials of various textures. These values are provided to exemplify the processes involved and would differ at an actual site. The oxygen concentration in the water can be increased by using oxygen rather than air, which would also reduce the volumes of recirculated water required.

Hydrogen peroxide is an alternative source of oxygen in bioreclamation. Iron or an organic catalyst may be used to decompose the hydrogen peroxide to oxygen. The rate at which hydrogen peroxide decomposes to oxygen must be controlled to limit the formation of bubbles that could lead to gas blockage and the loss of permeability. Hydrogen peroxide may mobilize metals such as lead and antimony, and if the water is hard, magnesium and calcium phosphates can precipitate and plug the injection well or infiltration gallery. To determine the microorganism's hydrogen peroxide tolerance level, laboratory studies are performed.

14.6.3 Permeable Reactive Treatment Walls

A permeable reactive barrier (PRB) contains or creates a reactive treatment zone oriented in such a way (i.e., perpendicular to ground-water flow direction) as to intercept and react with contaminants dissolved in ground water. The U.S. EPA (1998a/T14.9) provides a thorough review

of PRBs and associated applications for ground-water remediation. Additional references relating to PRBs can also be found in [Table 14.9](#).

Ground water moves through the PRB under its natural gradient, removing contaminants by physical, chemical, and biological processes. PRBs are typically installed as permanent structures across the flow path of a contaminant plume, while some have been installed as *in situ* reactors that are readily accessible to facilitate the removal and replacement of reactive media. PRBs are becoming increasingly attractive for certain recalcitrant organics (i.e., trichloroethylene (TCE), perchloroethylene (PCE), and carbon tetrachloride (CCl_4)) and metals (i.e., Cr^{+6} , U, and acid-mine drainage) because the net present value (NPV) of potentially large capital construction costs are moderated by lower long-term operation and maintenance costs, compared to many conventional mechanical treatment methods.

The majority of PRBs installed use zero valent iron or $\text{Fe}(0)$ as the reactive media to reduce contaminants to nontoxic or immobile species. PRBs typically rely on redox reactions to facilitate the reduction of the contaminant species while promoting the concomitant oxidation or corrosion of $\text{Fe}(0)$ to Fe^{+2} . In the case of organics, $\text{Fe}(0)$ PRBs can reductively dehalogenate TCE to ethene. They can also reductively precipitate anions and oxyanions, such as converting soluble $\text{Cr}(\text{VI})$ oxides to insoluble $\text{Cr}(\text{III})$ hydroxides. In addition to iron and other metals (i.e., Ni, Al, Zn, Sn, and Mg) being used in walls, organic materials are being used as reactive media in some PRBs to remediate nitrates and sulfates. Dating back to the early 1990s, laboratory and field results have shown that rates of transformation of these and many other contaminants are sufficiently rapid for PRBs to be successfully used as full-scale remediation systems.

Full-scale PRBs are currently being built in two basic configurations, the funnel-and-gate and the continuous-wall PRB. Both methods require some degree of excavation with trenching depths currently limited to 70 ft or less. Innovative techniques such as deep soil mixing, injection of slurries, hydrofracturing, etc., may prove beneficial for installing deeper PRBs. The funnel-and-gate design uses impermeable walls (e.g., sheet piling, slurry walls) as a “funnel” directing contaminated ground water toward the highly permeable “gate” structure containing the reactive media. The continuous wall, as the name suggests, has the reactive media transecting the entire width of contaminant plume. In both designs it is important to keep the reactive zone permeability at minimum equal or greater than that of the native aquifer to avoid short-circuiting ground-water flow around the reactive zone.

Prior to the installation of a PRB, several issues should be addressed to ensure long-term viability of using this technology. These include the nature of the contaminants to be treated and the availability of reactive media that can transform the contaminant(s) yet remain reactive *in situ* for relatively long time periods. For contaminants of unknown treatability, ground water of unknown geochemistry, or media of unknown reactivity, addressing these issues will require laboratory work at both the bench and column scales. The mobility, toxicity, and stability of the reaction transformation products must be assessed. If these transformation products are regulated compounds, the contaminated ground water moving through the PRB needs to have a sufficient retention time to either immobilize or transform them to innocuous compounds.

Since PRB technology relies on passive treatment and there is no mechanical advantage, a thorough understanding of the site hydrogeology and plume boundaries is needed prior to field implementation. The hydrogeologic characterization needs to yield information suitable for determining horizontal ground water flow through the reactive zone. This is necessary to determine the contaminant residence time per unit thickness of reactive media, which when combined with the contaminant transformation rate, determines the total thickness of the reactive media required. Once installed, the PRB should be carefully monitored for both compliance and performance: compliance to ascertain that contaminant cleanup goals are being met, and performance to assess whether the PRB emplacement is meeting the design criteria and longevity expectations.

14.6.4 Phytoremediation

Phytoremediation is a term applied to a variety of technologies that use plants for the transformation, degradation, or extraction of contaminants from the subsurface. There are a number of techniques that are often referred to as phytoremediation; however, the mechanism for achieving contaminant removal or risk reduction may be different. In general, phytoremediation refers to the use of plant-based environmental remediation technologies rather than a specific application. The U.S. EPA (2000/T14.9) provides an overview and informative evaluation of phytoremediation, including discussion on applications, mechanisms, system design, treatability and evaluation, and case studies. Additional references relating to phytoremediation can be found in [Table 14.9](#).

Phytoremediation applications can be classified based on the contaminant fate (e.g., extraction, containment, or degradation) or the mechanism involved (e.g., volatilization, transformation, biotic or abiotic degradation, or transpiration). Contaminants that have been evaluated with regard to phytoremediation include polycyclic aromatic hydrocarbons (PAHs), organic compounds, chlorinated solvents, metals, radionuclides, pesticides, phenols, and polychlorinated biphenyls (PCBs). Specific mechanisms and applications will be discussed below. These mechanisms include phytoextraction, rhizofiltration, phytostabilization, rhizodegradation, phytodegradation, and phytovolatilization.

Phytoextraction is a term applied to the uptake and translocation of contaminants by plants. Specific plants are planted that are known to accumulate contaminants in the shoots and leaves of the plants. The contaminants are often removed by harvesting the aboveground portion of the plants. An advantage is that a smaller volume of material is required for disposal compared to the extraction of soil or other media. This technique is most often applied to soils contaminated with metals.

Rhizofiltration occurs when contaminants in solution around the root zone are adsorbed into the roots or precipitated onto the plant roots due to biotic or abiotic processes. The contaminants may be taken up in the plant, concentrated, or translocated within the plant. Rhizofiltration is a type of contaminant containment in which the contaminants are immobilized or accumulated on the roots or within the plant. By physically removing the plants, the contaminants can be removed. Contaminants that have been evaluated include metals (zinc, nickel, copper, cadmium, and lead) and radionuclides (cesium, strontium, and uranium).

Phytostabilization is used in the treatment of soils, sediments, and sludges by immobilizing contaminants in the soil through adsorption onto roots or precipitation of contaminants within the root zone of plants. Root-zone chemistry and microbiology play an important role in phytostabilization of metals (arsenic, cadmium, chromium, copper, mercury, lead, and zinc). A disadvantage of phytostabilization is that the contaminants remain in place and are not removed directly. This may require long-term monitoring and maintenance to prevent the unwanted future release of contaminants to the environment.

Rhizodegradation is the actual transformation of a contaminant to breakdown products due to microbial activity within the root zone. This is often termed *root-zone biodegradation* where the roots give off exudates (compounds produced by plants and released through the roots). These exudates include sugars, amino acids, organic acids, fatty acids, enzymes, and other compounds. An advantage of rhizodegradation is that the contaminants are degraded or transformed *in situ*. Additionally, mineralization can occur where the contaminant is completely transformed to carbon dioxide and water as end products. However, the establishment of an extensive root zone may require time, and the root zone may be limited due to the soil moisture conditions. Another disadvantage is that root exudates might promote the growth of a microbial population that does not have the capability to degrade the target compounds. Additionally, these microorganisms may outcompete degraders for available nutrients. A wide range of compounds have been studied with regard to rhizodegradation, including total petroleum hydrocarbons, polycyclic aromatic hydrocarbons, benzene, toluene, ethylbenzene, xylenes, and chlorinated solvents.

Phytodegradation is the breakdown of contaminants taken up by plants through metabolic processes within the plants. Additionally, enzymes produced by the plant may break down target contaminants externally. The main mechanism for phytodegradation is plant uptake and metabolism. Phytodegradation is most appropriate for large soil areas with shallow contamination. A number of compounds have been evaluated with regard to phytodegradation, including chlorinated solvents, herbicides, insecticides, munitions, and phenols.

Phytovolatilization is the uptake and transformation of a contaminant within a plant with the release of the contaminant itself, or transformation product, to the atmosphere through plant transpiration.

The application of phytoremediation at a site is largely determined by site conditions and the remedial action objectives. Clearly, the use of plants as a treatment technology warrants sites with relatively shallow ground water with the necessary soil conditions to support phytoremediation. Often, phytoremediation is used as a source control technology where plants are planted and cultivated to intercept a shallow, contaminated ground-water stream. An advantage of using plants as a means of source control is that an expensive, engineered system does not need to be installed, leading to lower costs. The effective surface area of roots can penetrate and come in contact with a larger volume of contaminants than if several pumping wells were installed. A disadvantage of using plants for source control is that water uptake is variable and fluctuates with seasonal and climatic changes. Additionally, ground-water uptake is limited by the depth of the root zone.

Another application of phytoremediation is the use of an evapotranspiration (ET) cover or phytoremediation cover. An evapotranspiration cover consists of a cover of soil and plants to minimize water infiltration over a lower level of materials that present an environmental risk. Risk reduction is achieved by isolation of hazardous contaminants that may pose an environmental risk. An ET cover consists of a monolithic layer of soil with sufficient thickness to prevent the downward migration of infiltrated water. Vegetative grasses are also planted to assist with the uptake and storage of water.

A phytoremediation cover is similar to the ET cover except that plants are additionally utilized to aid in the degradation of subsurface contamination. Risk reduction is now a combination of the isolation of contaminants and enhanced degradation by the plants. Mechanisms include water uptake, root-zone degradation, and plant metabolism and transformation.

14.6.5 Enhanced Natural Attenuation

Natural attenuation (NA) of contaminants is the natural degradation and transformation of dissolved contaminants in the environment by the assimilative capacity of a ground-water system. In general, NA is the observed reduction on contaminant concentration as contaminants migrate away from the initial source zone. The observed reduction on contaminant concentration can be brought about by several mechanisms, including dilution, dispersion, sorption, volatilization, and biotic and abiotic transformations. Wiedemeier et al. (1999/T14.9) present a comprehensive discussion on NA of fuels and chlorinated solvents in the subsurface.

Enhanced natural attenuation (ENA) is the addition of a selected chemical constituent(s) to the subsurface to stimulate one or more of the NA mechanisms, most notably, biotic transformations. Electron acceptors or donors can be added to the subsurface to enhance the transformation of target compounds. Common electron acceptors associated with the microbial metabolism of organic contaminants include oxygen, nitrate, Mn(IV), Fe(III), sulfate, and, in some cases, carbon dioxide (Wiedemeier et al., 1999/T14.9). Oxygen-releasing compounds such as magnesium peroxide provide oxygen in an aquifer when hydrated. Patented formulations such as ORC (Oxygen Release Compound) have been developed to provide a slow-release source of oxygen for aerobic metabolism of such compounds as benzene, toluene, ethylbenzene, xylene, polycyclic aromatic hydrocarbons, and other light petroleum hydrocarbons (Koenigsberg and Norris, 1999/T14.9). Slow-release compounds

are attractive in that the treatment approach avoids costly capital investments and operational and maintenance costs. ORC can be injected as a slurry and remain active in place from 4 to 12 months.

Reductive dechlorination has been shown to be the primary transformation mechanism for chlorinated ethenes. The presence of electron donors can often be the controlling factor in the rate of transformation of chlorinated solvents. In an effort to enhance the natural attenuation of chlorinated solvents, hydrogen-releasing compounds have been developed and marketed. Patented formulations such as HRC (Hydrogen Release Compound) provide a slow-release source of hydrogen as an electron donor in the subsurface. Additionally, a variety of soluble compounds such as sugars, lactic acid, and alcohols can be added to a contaminated aquifer zone to drive down the redox potential and liberate hydrogen. However, the more soluble donors often must be repeatedly injected. HRC can be injected as a slurry or syrup and provide an active release of hydrogen from 6 to 12 months. A significantly less expensive (Harkness 2000/T14.9) alternative to HRC, vegetable oil, has also been evaluated as a potential long-term source of hydrogen to stimulate reductive dechlorination. During a 6-month evaluation, subsequent to the addition of vegetable oil in the source area of a 160-acre chlorinated solvent plume, Boulicault et al. (2000/T14.9) observed an increase in daughter products (cis-1,2-dichloroethene and vinyl chloride) relative to the parent compound trichloroethylene, indicating that the reaction had been stimulated.

14.7 GUIDE TO MAJOR REFERENCES

Table 14.9 provides an index to major references that focus on ground-water remediation in the categories of (1) source controls and (2) ground-water and leachate treatment. The references on cover and liner systems are especially important when designing waste disposal facilities for the prevention of ground-water contamination.

Table 12.7 provides an index to major references that address broader aspects of remediation of contaminated soil and ground water. Many of the conference series identified in Table 5.12 contain useful papers on ground-water treatment and remediation, especially the annual NGWA National Outdoor Action Conference, the annual NGWA/API Petroleum Hydrocarbons and Organic Chemicals Conference, and the various conference series published by the Hazardous Materials Control Resources Institute. Table 12.7 identifies additional conference proceedings (note especially the Battelle bioremediation and chlorinated/recalcitrant compounds series) that focus on remediation of contaminated ground water. Currently, many remedial techniques are being used and evaluated for cleanup of contaminated ground water.

From 1992 to 2002 the U.S. EPA Technology Innovation Office published a newsletter titled *Ground Water Currents*, which provided information on innovative ground-water treatment technologies. See Section 12.5, which provides information on the successor newsletter, and also information on various documents that are available as part of U.S. EPA's Superfund Innovative Technology Evaluation (SITE) program.

Table 14.9 Index to Major References on Ground Water and Leachate Treatment and Remediation

Topic	References
General	Bedient (1999, 2000), Delleur (1998), National Research Council (1994), Testa and Winegardner (2000), U.S. EPA (1978, 1988a, 1989d, 1992b, 1993), Willis and Yeh (1987), Wilson et al. (1976), see, generally, soil and ground water references and the conference and symposium series identified in Table 12.7; <u>Cleanup Standards</u> : Buonicore (1996/T12.7), Oliver et al. (1993/T12.7), U.S. EPA (1992c), WEF (1994a/T12.7); <u>Innovative Technologies</u> : U.S. EPA (1999/T12.7)
Natural Attenuation	Brady et al. (1997), U.S. EPA (1996b, 1998, 1999a, 1999b), Wiedemeier et al. (1999)
Source Controls	
General Design	Atlantic Research Corporation (1980), Bagchi (1990), Chapman (1993), Tolman et al. (1978), U.S. EPA (1988b), VanZyl et al. (1987)
Cover/Liner Systems	Daniel and Estornell (1991), Fung (1980); <u>Cover Systems</u> : Barnes and Rogers (1988), Dwyer et al. (1986), Gilbert and Murphy (1987), Horz (1986), Landreth et al. (1991), Lutton (1982, 1987), Lutton et al. (1979), McAneny et al. (1985b), U.S. EPA (1987a); <u>Liner Systems</u> : Anderson et al. (1991), ASTM (1994), Brown et al. (1987), Daniel et al. (1991), Matrecon (1988), Mitchell et al. (1989), Telles et al. (1988), U.S. EPA (1983, 1985a, 1985b, 1985c, 1985d, 1986a, 1986b, 1987b, 1989c), Wright et al. (1987); <u>Geosynthetics</u> : Bellen et al. (1987), Goydan et al. (1990), Horz (1986), Koerner (1990), Lord and Koerner (1990), Richardson and Koerner (1987), SAI Corp. (1993), Schwoppe et al. (1985), Telles et al. (1988), U.S. EPA (1989b, 1989c, 1991), Wright et al. (1987); <u>Chemical Effects/Compatibility</u> : Bellen et al. (1987), Brown (1988), Goydan et al. (1990), Schwoppe et al. (1985)
Barriers	Fung (1980); <u>Grouting</u> : Bodocsi et al. (1988), Bowen (1981), May et al. (1986), Spooner et al. (1984); <u>Slurry Walls</u> : Millet and Perez (1981), Ryan (1980), Xanthakos (1979)
Hydrodynamic Controls	Gorelick et al. (1993), Horz (1986); <u>Leachate Plume Management</u> : Repa and Doerr (1985), U.S. EPA (1989c); <u>Surface Impoundments</u> : Johnson and Anderson (1988), Mitchell et al. (1989), Richardson and Koerner (1987)
Ground Water/Leachate Treatment	
Drinking Water/Wastewater	Fair et al. (1968); <u>Drinking Water</u> : U.S. EPA (1989a); <u>Wastewater</u> : Barnett (1998), Benefield et al. (1982), Cherminisinoff (1994), Faust and Aly (1998), Grady et al. (1998), Liu and Liptak (1998), Metcalf and Eddy (1979), Mueller (2002 — aeration), Patterson (1978), Sundstrom and Klei (1979), U.S. EPA (1992a); <u>Industrial Wastewater</u> : Eckenfelder (1997), Eckenfelder and Musterman (1998), Patterson (1985), Stephenson and Blackburn (1997)
Contaminated Ground Water	<u>Texts/Reports</u> : Ahlert and Kosson (1988), Nyer (1989), Shuckrow et al. (1986), U.S. EPA (1994a, 1995a, 2001b — fractured rock); <u>Review Papers</u> : Nielsen (1983); <u>Cleanup Standards</u> : Buonicore (1996), Oliver et al. (1993/T12.7), WEF (1994a)
Bioremediation	Lee et al. (1988), see also references on soil and ground-water bioremediation in Table 12.7; <u>In Situ Bioremediation</u> : Semprini et al. (1987), Sims et al. (1992)
Pump and Treat	Cohen et al. (1994, 1997), Keely (1989), Mercer et al. (1990), Palmer and Fish (1992), U.S. EPA (1996a, 2001a); <u>Extraction Methods</u> : U.S. EPA (1989d, 1992b, 1994b)
<i>In Situ</i> Treatment	Fields et al. (2002 — air sparging), Place et al. (2001 — NAPL bioslurping); <u>Permeable Reactive Treatment Walls</u> : Battelle (1997), Benner et al. (1997, 2000), Bennett et al. (1997), Blowes and Ptacek (1992), Blowes et al. (1997), Eykholt (1997), Gavaskar et al. (1998), Hocking (1998), McGregor et al. (1999), McRae et al. (1999), Puls and Blowes (2000), Puls et al. (1999), Roberts et al. (1996), Shoemaker et al. (1996), U.S. EPA (1995b, 1998a, 1999c), Teel et al. (1998); <u>Wetlands</u> : Means and Hinchee (2000), Mulamoottil et al. (1998), Nearing and Brauning (2002), Odum (2000 — heavy metals), see also references for bioremediation above and UST remediation (Table 12.7)

Table 14.9 Index to Major References on Ground Water and Leachate Treatment and Remediation (*Continued*)

Topic	References
Leachate Collection/Treatment	U.S. EPA (1995a); <u>Collection</u> : Ghassemi et al. (1985), Kirkham et al. (1986), Pohland and Harper (1986), U.S. EPA (1985c, 1986a, 1989c, 1994b); <u>Landfill</u> : Mulamootil et al. (1998 — wetlands); <u>Hazardous Waste</u> : Ahlert and Kosson (1988), McArdle et al. (1987), Park (1986), Shuckrow et al. (1986)
Phytoremediation	Alleman and Leeson (1999), American Institute of Chemical Engineers et al. (1999), Fiorenza et al. (2000), Kruger et al. (1997), McCutcheon and Schnoor (2003), Nyer (2001), Raskin and Ensley (1999), Spain et al. (2000), Suthersan (1997, 2002), Terry and Banuelos (2000), U.S. EPA (2000), Wickramanayake and Hinchee (1998), Wickramanayake et al. (2000)
Leachate Chemistry	<u>Hazardous Waste</u> : Bramlett et al. (1987); <u>Municipal Waste</u> : Kinman et al. (1986), Pohland and Harper (1986, 1987), Williams et al. (1987)
Specific Methods	<u>Air Stripping</u> : Hinchee (1994), Noonan and Curtis (1990); <u>GAC</u> : Cheremisinoff and Ellerbusch (1978), Noonan and Curtis (1990)
Specific Contaminants	See Table 12.7

Table 14.9 References (Appendix F contains references for figure and table sources.)

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* See Preface for information on how to obtain documents from CERL and NTIS.

APPENDIX A

Summary Information on Major Subsurface Characterization and Monitoring Techniques

Table A.1 through Table A.13 in this appendix are method tables taken from EPA’s *Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide* (Boulding, 1993), which contains one- to two-page summary descriptions of more than 280 specific field methods. This two-volume guide was still in print as of early 2003 and can be obtained at no cost from U.S. EPA’s National Service Center for Environmental Publications (see Preface for information on how to obtain documents from the NSCEP). This appendix is intended to serve as a convenient summary of methods covered in that guide. *All section numbers in tables and footnotes refer to locations in the EPA guide*, where more detailed information about specific methods can be found. There have been a few new developments in instrumentation that are not covered in the EPA guide. Sections 6.5, 7.1.1, and 7.1.2 discuss recent developments in measuring matric potential, moisture content, and vadose zone hydraulic properties. Section 7.3.2 identifies recent developments in single- and multiple-well tests, including hydraulic tomography. Section 9.2.2 discusses recent enhancements to the hollow-stem auger and a variant of the air rotary called cryogenic drilling, and Section 9.5.4 discusses recent developments in multilevel ground water sampling, including diffusion samplers. Below is a list of the tables in this appendix and the pages on which they are located.

Appendix B provides a listing and comprehensive index of more than 500 ASTM standards covering potential field and laboratory methods for sampling and characterization of soil, ground water, and waste materials. Table A.14 provides a shorter list of specific ASTM standards cited in this handbook.

Table	Page
A.1	Summary Information on Remote Sensing and Surface Geophysical Methods
A.2	Characteristics of Borehole Logging Methods
A.3	Summary Information on Vadose Zone Water State Measurement and Monitoring Methods
A.4	Summary Information on Vadose Hydraulic Conductivity Techniques
A.5	Summary Information on Vadose Zone Water Budget Characterization Methods
A.6	Summary Information on Ground Water Level/Pressure Measurement
A.7	Summary Information on Aquifer Test Methods
A.8	Summary Information on Drilling Methods
A.9	Summary of Handheld Soil Sampling Devices
A.10	Summary of Major Types of Power-Driven Samplers
A.11	Summary Information on Soil-Solute Monitoring and Sampling Methods
A.12	Summary Information on Ground-Water Sampling Devices
A.13	Summary Information on Sample Processing/Analytical Techniques
A.14	ASTM Standard Methods Cited in This Handbook

Table A.1 Summary Information on Remote Sensing and Surface Geophysical Methods

Technique	Soils/ Geology	Leachate	Buried Wastes	NAPLs	Penetration Depth (m) ^a	Cost ^b	Section/Tables
Airborne Remote Sensing and Geophysics							
Visible Photography +	Yes	Yes ^c	Possibly ^d	Yes ^c	Surf. only	L	1.1.1/Tb 1.1.1
Infrared Photography +	Yes	Yes ^c	Possibly ^d	Yes ^c	Surf. only	L-M	1.1.1/Tb 1.1.1
Multispectral Imaging	Yes	Yes ^c	No	Yes ^c	Surf. only	L	1.1.1/Tb 1.1.1
Ultraviolet Photography	Yes	Yes ^c	No	Yes ^c	Surf. only	L	1.1.2/Tb 1.1.1
Thermal Infrared Scanning	Yes	Yes (T)	Possibly ^d	Possibly	Surf. only	M	1.1.3
Active Microwave (Radar) +	Yes	Possibly	No	Possibly	0.1–2	M	1.1.4
Airborne Electromagnetics	Yes	Yes (C)	Yes	Possibly	0–100	M	1.1.5
Aeromagnetics	Yes	No	Yes	No	10s–100s	M	1.1.6
Surface Electrical and Electromagnetic Methods							
Self Potential	Yes	Yes (C)	Yes	No	S 10s	L	1.2.1
Electrical Resistivity +	Yes	Yes (C)	Yes (M)	Possibly	S 60 (km)	L-M	1.2.2, 9.1.1/Tbs 1.2, 1.3, 1.2.1
Induced Polarization	Yes	Yes (C)	Yes	Possibly	S km	L-M	1.2.3
Complex Resistivity	Yes	Yes (C)	Yes	Yes	S km	M-H	1.2.3
Dielectric Sensors	Yes	Yes (C)	No	Possibly	S 2 ^e	L-M	6.2.3/Tb 6.1
Time Domain Reflectometry	Yes	Yes (C)	No	Yes	S 2 ^e	M-H	6.2.4/Tb 6.1
Electromagnetic Induction +	Yes	Yes (C)	Yes	Possibly	S 60(200)/C 15(50)	L-M	1.3.1/Tbs 1.2, 1.3, 1.3.1
Transient Electromagnetics	Yes	Yes (C)	Yes	No	S 150 (2000+)	M-H	1.3.2/Tb 1.3.1
Metal Detectors	No	No	Yes	No	C/S 0–3	L	1.3.3/Tbs 1.2, 1.3
VLF Resistivity	Yes	Yes (C)	Yes	No	C/S 20–60	M-H	1.3.4
Magnetotellurics	Yes	Yes (C)	No	No	S 1000+	M-H	1.3.5
Surface Seismic and Acoustic Methods							
Seismic Refraction +	Yes	Yes	No	No	S 1–30 (200+)	L-M	1.4.1/Tbs 1.2, 1.3
Shallow Seismic Reflection +	Yes	No	No	No	S 10–30 (2000+)	M-H	1.4.2

Continuous Seismic Profiling	Yes	No	No	No	C 1–100	L-M	1.4.3
Seismic Shear/Surface Waves	Yes	No	No	No	S 10s–100s	M-H	1.4.4
Acoustic Emission Monitoring	Yes	No	No	No	S 2 ^e	L	1.4.5
Sonar/Fathometer	Yes	Yes	No	No	C no limit	L-H	1.4.6

Other Surface Geophysical Methods

Ground-Penetrating Radar +	Yes	Yes (C)	Yes	Yes	C 1–25 (100s)	M	1.5.1/Tbs 1.2, 1.3
Magnetometry +	No	No	Yes (F)	No	C/S 0–20 ^f	L-M	1.5.2/Tbs 1.2, 1.3
Gravity	Yes	Yes	No	No	S 100s+	H	1.5.3
Radiation Detection	No	No	Yes (nuclear)	No	C/S near surface	L	1.5.4

Near-Surface Geothermometry

Soil Temperature	Yes	Yes (T)	No	No	S 1–2 ^e	L	1.6.1
Ground-Water Detection	Yes	Yes (T)	No	No	S 2 ^e	L	1.6.2
Other Thermal Properties	Yes	No	No	No	S 1–2 ^e	L-M	1.6.3

Note: All ratings are approximate and for general guidance only. Boldface = most commonly used methods at contaminated sites; + = covered in Superfund Field Operations Manual (U.S. EPA, 1987a); (C) = plume detected when contaminant(s) change conductivity of ground water; (F) = ferrous metals only; (T) = plume detected by temperature rather than conductivity.

^a S = station measurement; C = continuous measurement. Depths are for typical shallow applications; () = achievable depths.

^b Ratings are very approximate: L = low, M = moderate, H = high.

^c If leachate or NAPLs are on the ground or water surface or indirectly affect surface properties, see Table 1.1.1; field confirmation required.

^d Disturbed areas that may contain buried waste can often be detected on aerial photographs.

^e Typical maximum depth; greater depths possible, but sensor placement is more difficult and cable lengths must be increased.

^f For ferrous metal detection, greater depths require larger masses of metal for detection; hundreds of meters depth can be sensed when using magnetometry for mapping geologic structure.

Table A.2 Characteristics of Borehole Logging Methods

Log Type/Section	Casing ^a	Min. Diam. ^b	Borehole Fluid	Radius of Measurement	Required Correction
Electrical Logs					
Spontaneous Potential (3.1.1)	Uncased only	1.5–3.0"	Conductive fluid	Near borehole surface	Drilling fluid resistivity and borehole diameter for quantitative uses
Single-Point Resistance (3.1.2)	Uncased only	1.5–2.0"	Conductive fluid	Near borehole surface	Not quantitative; hole diameter effects significant
Fluid Conductivity (3.1.3)	Uncased or screened	2.0–2.5"	Conductive fluid	Within borehole	Calibration with fluid of known salinity; temperature correction
Resistivity (3.1.4)	Uncased only	2.0–5.5"	Conductive fluid	<1.0–60"	Drilling fluid resistivity, borehole diameter, and temperature log for quantitative uses
Dipmeter (3.1.5)	Uncased only	6.0"	Conductive fluid	Near borehole surface	Orientation; minimum of 6" diameter required for accurate joint/fracture characterization
Induced Polarization (3.1.6)	Uncased only	2.0"	Conductive fluid	2.0–4.0'	Hole diameter
Cross-Well AC Voltage (3.1.6)	Uncased only	?	Wet or dry	10s to 100s of meters	Borehole deviation
Electromagnetic Logs					
Induction (3.2.1)	Uncased or nonmetallic	2.0–4.0"	Wet or dry	30"	Effect of hole diameter and mud negligible
Borehole Radar (3.2.2)	Uncased or nonmetallic	2.0–6.0"	Wet or dry	Meters	Borehole deviation (crosshole)
Dielectric (3.2.3)	Uncased or nonmetallic	5.0"	Wet or dry	30"	Conductive material skin depth; chlorine interference
Nuclear Magnetic Resonance (3.2.4)	Uncased only	7.0"	Required	1.5'	Borehole fluid
Surface-Borehole CSAMT (3.2.4)	Uncased only (?)	?	Wet or dry(?)	?	?
Nuclear Logs					
Natural Gamma (3.3.1)	Uncased or cased	1.0–2.0"	Wet or dry	6.0–12.0"	None for qualitative uses; hole diameter, casing (thickness, composition, and size), and drilling fluid density for quantitative uses
Gamma-Gamma (3.3.2)	Uncased or cased	2.5"	Wet or dry	6.0"	Same as natural gamma with addition of formation fluid and matrix density corrections

Neutron (3.3.3)	Uncased or cased	1.5–4.5"	Wet or dry	6.0–12.0"	Same as natural gamma with addition of temperature, fluid salinity, and matrix composition corrections
Gamma Spectrometry (3.3.4)	Uncased or cased	2.0–4.0"	Wet or dry	6.0–12.0"	Similar to natural gamma
Neutron Activation (3.3.5)	Uncased or cased	2.0–4.0"	Wet or dry	< Neutron	?
Neutron Lifetime (3.3.6)	Uncased or cased	2.0–4.0"	Wet or dry	< Neutron	?

Acoustic and Seismic Logs

Acoustic-Velocity/Sonic^c (3.4.1)	Uncased or bonded metallic	2.0–4.0"	Required	Depends on frequency and rock velocity; several feet	Hole diameter, formation fluid, and matrix velocity corrections for quantitative uses
Acoustic Waveform ^c (3.4.2)	Uncased or bonded metallic	2.5–3.0"	Required	> Sonic	Same as sonic
Acoustic Televiewer (3.4.3)	Uncased only	3.0" min., 16.0" max.	Required	Borehole surface	Large number of equipment adjustments required during operation (calibration of magnetometer), borehole diameter response, borehole deviation
Surface-Borehole Seismic (3.4.4)	Uncased or bonded cased	2.5–4.0"	Wet or dry	Depends on geophone configuration	Borehole deviation, correction for geometric spreading of source energy; geophones must be locked in dry holes
Geophysical Diffraction Tomography (3.4.5)	Uncased or nonmetallic	2.5–4.0"	Wet	100'	Borehole deviation
Cross-Borehole Seismic (3.4.6)	Cased or uncased	2.0–3.0"	Wet or dry	Depends on borehole spacing	Borehole deviation

Miscellaneous Logging Methods

Caliper (3.5.1)	Uncased or cased	1.5"+	Wet or dry	Arm limit (usually 2.0–3.0')	None
Temperature (3.5.2)	Uncased or cased ^d	2.0"	Required	Within borehole	Calibration to known standard
Mechanical Flowmeter (3.5.3)	^e	2.0–4.0"	Required	^e	Borehole diameter for velocity and volumetric logging
Thermal Flowmeter (3.5.4)	^e	2.0"	Required	^e	Borehole diameter for velocity and volumetric logging
EM Flowmeter (3.5.5)	^e	2.0"	Required	^e	Borehole diameter for velocity and volumetric logging
Single-borehole flow tracing (3.5.6)	^e	1.75"+	Required	^e	Changes in flow field with time
Colloidal Boroscope (3.5.7)	^e	2.0"	Required	^e	None
Television/Photography (3.5.7)	Uncased or cased	2.0"+	Wet or dry	Borehole surface	None

Table A.2 Characteristics of Borehole Logging Methods (Continued)

Log Type/Section	Casing ^a	Min. Diam. ^b	Borehole Fluid	Radius of Measurement	Required Correction
Gravity (3.5.8)	Uncased best	6.0"	Wet or dry	10s to 100s of meters	Borehole diameter/inclination; other usual gravity corrections
Magnetic/Magnetic Susceptibility (3.5.8)	Uncased or nonmetallic	?	Wet or dry	1.0–2.0'	Hole diameter correction
Well Construction Logs					
Casing Collar Locator (3.6.1)	Steel casing	2.0"+	Wet or dry	Casing collar, thickness	None
Cement and Gravel Pack Logs (3.6.2)	Cased	See specific logging methods discussed in Section 3.6.2			
Borehole Deviation (3.6.3)	Uncased	Varies	Wet or dry	Borehole surface	Magnetic declination
Fluid/Gas Chemical Sensors					
Eh, Ph Probes (5.5.4)	Uncased/screened	1.0"	Required	Within borehole	Calibration to known standards
Ion-Selective Electrodes (5.5.5)	Uncased/screened	1.0"	Required	Within borehole	Calibration to known standards
Fiber-Optic Chemical Sensors (5.5.6)	Uncased/screened	<2.0"	Wet or dry	Within borehole	Calibration to known standards
Other Chemical Sensors (10.6.5)	Uncased/screened	<1.0"–2.0"	Wet or dry	Within borehole	Calibration to known standards

Note: Information for general guidance only. Boldface = most frequently used techniques in ground-water investigations.

^a Unless otherwise specified, either plastic or steel casing is possible.

^b Indicates the range of minimum diameters for commercially available probes based on best available information. Various sources were used, with the survey by Adams et al. (1983) being the main source.

^c Wheatcraft et al. (1986) indicate that acoustic logs are suitable only for uncased boreholes. However, Thornhill and Benefield (1990) report using them for mechanical integrity tests of steel-cased injection wells.

^d Wheatcraft et al. (1986) indicate that casing is allowable for temperature logs; Benson (1991) indicates that casing should not be used. Uncased holes are required for identification of high-permeability zones. Cased hole uses would include measurement of geothermal gradient and cement bond logs (see Section 3.6.2).

^e Flow measurements are usually made in uncased holes or screened intervals of cased holes. Radius of measurement depends on the permeability and whether natural or induced flow is measured. Natural flow will measure the properties of several well diameters; pumping will measure properties up to 25 to 35 well diameters (Taylor, 1989).

Table A.3 Summary Information on Vadose Zone Water State Measurement and Monitoring Methods

Method	Property Measured	Accuracy/Range	Sections
Vadose Zone Soil Water Potential Measurement^a			
Porous Cup Tensiometers	Capillary pressure	0 to –85 kPa ^b 0 to –80 kPa ^c	6.1.1
Thermocouple Psychrometers	Relative humidity	–200 to –8000 kPa ^b –100 to –5000 kPa ^c	6.1.2
Resistance Sensors	Resistance	–50 to –1500 kPa ^c	6.1.3
Gypsum Blocks	Resistance	0 to –30 kPa ^b	6.1.3
Fiberglass/Nylon Cells	Resistance	No limits ^b	6.1.3
Electrothermal Methods	Heat transfer	0 to –200 kPa	6.1.4
Osmotic Tensiometers	Osmotic + pressure potential	0 to –1500 kPa ^b	6.1.5
Filter Paper Method	Water content	–10 to –100,000 kPa	6.1.6
Electro-Optical Sensors	Optical properties	0 to –2400 kPa	6.2.6
Water Activity Meter	Relative humidity	0 to –31,600 kPa	6.1.7
Vadose Zone Soil Water Content Measurement^a			
Gravimetric	Weight	^d	6.2.1
Gamma-Gamma	Radiation	^d	6.2.2, 3.3.2
Neutron Moisture Probe	Radiation	^d	6.2.2, 3.3.3
Dielectric Sensors	Dielectric	^d	6.2.3
Time Domain Reflectometry	Dielectric	^d	6.2.4
Nuclear Magnetic Resonance	Magnetic field	^d	6.2.5, 3.2.4, 10.6.3
Electro-Optical Sensors	Optical properties	^d	6.2.6
CAT Scan	Radiation	^d	6.2.7
Thermal Infrared	Remote sensing	^d	1.1.3
Active Microwave	Remote sensing	^d	1.1.4
Four-Electrode Method	Resistivity	^d	9.1.1
Salinity Sensors	Conductivity	^d	9.1.3
Electromagnetic Induction	Conductivity	^d	9.1.4
Other Vadose Zone Hydrologic Properties			
Soil Moisture–Potential–Conductivity Relationships			6.3.1
Water Sorptivity/Diffusivity			6.3.2
Available Water Capacity		0.1–1%	6.3.3

Note: Boldface = most commonly used methods.

^a Moisture content can be determined from measurement of soil water potential and vice versa by the use of a moisture characteristic curve, which relates matric potential to water content (Section 6.3.1). The pascal is the Standard International unit for measuring pressure used by the Soil Science Society of America. The bar is commonly used as a pressure unit in vadose zone investigations: 1 kPa = 1 cbar.

^b Indicated by Rehm et al. (1985).

^c Indicated by Bruce and Luxmoore (1986).

^d Most methods for measuring moisture content are accurate to around 1%. Gravimetric methods and nuclear methods can be accurate to 0.1% or less.

Table A.4 Summary Information on Vadose Hydraulic Conductivity Techniques^a

Technique	K_{fs} or K_{unsat}	K Direction ^b	Other Parameters Measured	Section	Tables
Infiltration (see also Sections 7.2.3, 7.2.5, 7.2.6, 7.3.1, 7.3.4)					
Seepage Meters	Saturated	Undefined	I	7.1.1	
Instantaneous Rate	Saturated	Undefined	I	7.1.1	
Impoundment Water Budget	Saturated	Undefined	I	7.1.1	
Sprinkler Infiltrometer	Saturated	Vertical	I	7.1.2	
Infiltration Test Basins	Saturated	Undefined	I	7.1.2	
Watershed Average	Undefined	Undefined	I	7.1.3	
Watershed Empirical Relations	Undefined	Undefined	I	7.1.3	
Infiltration Equations	Both	Vertical	I	7.1.4	7.5
Unsaturated Hydraulic Conductivity					
Instantaneous Profile	Unsaturated	Vertical	D, F, $K(\phi)$, R	7.2.1	7.3
Draining Profile Methods	Unsaturated	Vertical	D, F, $K(\phi)$, R, S	7.2.2	7.3
Tension Infiltrometers	Both	Vertical	I, D, F, $K(\phi)$, R, S	7.2.3	7.3
Crust-Imposed Steady Flux	Unsaturated	Vertical	I, F, $K(\phi)$	7.2.4	7.3
Sprinkler/Dripper Methods	Unsaturated	Vertical	I, F, $K(\phi)$, R, S	7.2.5	7.3
Entrapped Air Method	Unsaturated	Vertical	I, F	7.2.6	7.3
Parameter Identification	Both	Undefined	R	7.2.7	7.3
Empirical Equations	Both	Undefined	Varies	7.2.8	7.5
Column-Crust	Both	Vertical	F, $K(\phi)$	7.3.8	7.4
Saturated Hydraulic Conductivity above Shallow Water Table^c					
Cylinder Infiltrometers	Saturated	Vertical	I, S	7.3.1	7.4
Constant Head Borehole Infiltration	Saturated	Horizontal	S	7.3.2	7.4
Guelph Permeameter	Both	Vertical/Horizontal	$K(\phi)$, S	7.3.3	7.4
Air-Entry Permeameter	Both	Vertical	I, $K(\phi)$, S	7.3.4	7.2, 7.4
Double Tube	Saturated	Vertical	—	7.3.5	7.2, 7.4
Cylinder Permeameter	Saturated	Vertical	—	7.3.6	7.2, 7.4
Infiltration Gradient	Saturated	Vertical ^d	—	7.3.7	7.4
Cube	Saturated	Vertical/Horizontal	—	7.3.8	7.2, 7.4
Column/Monoliths	Saturated	Vertical	—	7.3.8	7.2, 7.4
Boutwell Method	Saturated	Vertical/Horizontal	—	7.3.9	
Velocity Permeameter	Saturated	Vertical	—	7.3.10	
Percolation Test	— ^e	— ^e	—	7.3.11	7.4
CP Porous Probe	Saturated	Horizontal	—	2.2.2	
Collection Lysimeter	Saturated	Vertical	F	9.3.1	
Saturated Hydraulic Conductivity above Deep Water Table^c					
USBR Single Well	Saturated	Undefined	—	7.4.1	
USBR Multiple Well	Saturated	Horizontal	—	7.4.2	
Stephens–Neuman Single Well	Saturated	Undefined	—	7.4.3	
Air Permeability	Saturated	Undefined	—	7.4.4	
Packer Tests	Saturated	Vertical/Horizontal	—	4.3.3	

Note: D = diffusivity; F = flux; I = infiltration; $K(\phi)$ = hydraulic conductivity-pressure head relationship; R = retention (pressure-moisture relationship); S = sorptivity.

^a Most methods for measuring or estimating unsaturated hydraulic conductivity also can be used to measure water flux in the vadose zone. Section 7.5 discusses the application of these and other methods for measuring soil water flux.

^b Directional ratings are qualitative in nature. Different references might give different ratings depending on site conditions and criteria used to define directionality.

^c These methods measure *field-saturated* or *satiated* hydraulic conductivity (K_{fs}), which is lower than *saturated* hydraulic conductivity, due to the presence of entrapped air.

^d Differentiation of vertical and horizontal is possible when used with double-tube method.

^e The percolation test does not provide an accurate measure of saturated hydraulic conductivity. See Table 7.4 for sources on information on the relationship between percolation test results and K_{sat} .

Table A.5 Summary Information on Vadose Zone Water Budget Characterization Methods

Technique	Parameters Measured	Manual/ Automatic	S/A/R	Section	Tables
Water-Related Hydrometeorological Measurements		A			
Sacramento Gauge	Rain	Manual	±1 mm ^a	8.1.1	8.2
Storage Gauge	Rain	Manual	±1 mm ^a	8.1.1	8.2
Automatic Wet/Dry Collectors	Rain/Snow	Either	±1 mm ^a	8.1.1	8.2
Weighing Gauge	Rain/Snow	Automatic	±1 mm ^a	8.1.2	8.2
Tipping Bucket Gauge	Rain	Automatic	±1 mm ^a	8.1.2	8.2
Float Gauge	Rain	Automatic	±1 mm ^a	8.1.2	8.2
			S/A/R		
Sling Psychrometer	Humidity	Manual	0.1/0.5/—	8.1.3	8.2
Aspirated Psychrometer	Humidity	Either	0.02/0.1/—	8.1.3	8.2
Thermocouple Psychrometer	Humidity	Either	?	6.1.2	6.1, 6.3
Mechanical Hygrometers	Humidity	Either	1.0/5.0/20–100%	8.1.4	8.2
Dew-/Frost-Point Hygrometer	Humidity	Either	0.05/0.25/—	8.1.4	8.2
Dew Cell/Probes	Humidity	Automatic	0.5/2.0/10–100%	8.1.4	8.2
Electric Hygrometers	Humidity	Either	0.5/2.0/5.0–98%	8.1.4	8.2
Diffusion Hygrometers	Humidity	?	?	8.1.4	8.2
Absorption Spectra Hygrometers	Humidity	?	?	8.1.4	8.2
Other Hydrometeorological Measurements		A/R			
Liquid-in-Glass Thermometer	Temperature	Manual	±0.5°C/–40 to +60 ^b	8.2.1	
Bi-Metal Thermometer	Temperature	Either	±0.5°C/–40 to +60 ^b	8.2.1	
Bourdon Tube Thermometer	Temperature	Either	±0.5°C/–40 to +60 ^b	8.2.1	
Thermocouple	Temperature	Either	±0.5°C/–40 to +60 ^b	8.2.2	
Metallic Resistance Bulb	Temperature	Either	±0.5°C/–40 to +60 ^b	8.2.2	
Thermistor	Temperature	Either	±0.5°C/–40 to +60 ^b	8.2.2	
Cup Anemometers	H wind speed	Either	1.0–50/±0.5m/sec ^a	8.2.3	8.2
Windmill Anemometers	V-H wind speed	Either	1.0–50/±0.5m/sec ^a	8.2.3	8.2
Pressure Anemometers	H wind speed	Manual	1.0–50/±0.5m/sec ^a	8.2.3	8.2
Hot-Wire Anemometer	V-H wind speed	Automatic	1.0–50/±0.5m/sec ^a	8.2.3	8.2
Acoustic Anemometer	V-H wind speed	Automatic	1.0–50/±0.5m/sec ^a	8.2.3	8.2
Wind Vanes	Direction	Either	0.5–50/±5°	8.2.4	8.2
Wind Cones	Direction	Manual	1.0–50/±0.5m/sec ^a	8.2.4	8.2
			S/A		
Mercury Barometer	Air pressure	Manual	?	8.2.5	
Altimeter	Air pressure	Manual	2 hPa/±0.2%	8.2.5	
Precision Aneroid	Air pressure	Either	0.5 hPa/?	8.2.5	
			A		
Thermopile Pyranometers	Global rad.	Automatic	±0.1–0.5 mW/cm ²	8.2.6	8.2
Bimetallic Pyranometer	Global rad.	Either	±1.0 mW/cm ²	8.2.6	8.2
Photovoltaic Pyranometer	Global rad.	Either	?	8.2.6	8.2
Net Radiometers	Net flux	Either	?	8.2.7	8.2
Pyrheliometers	Direct rad.	Either	?	8.2.7	8.2
Evapotranspiration (Water Balance Methods)			Accuracy		
Lysimeters	WE, SE, ET, T	Either	Moderate to high ^c	8.3.1	8.3
Soil Moisture Monitoring	SE, ET, T	Manual	Moderate to high ^c	8.3.2	8.3
Water Budget Methods	WE, SE, ET, T	Manual	Low to high	8.3.3	8.3
Evaporation Pans	WE	Manual	Moderate	8.3.4	8.3
Evaporimeter	SE	Manual	High ^c	8.3.5	
Atmometers	SE, T	Manual	Moderate	8.3.5	8.3
Chloride Tracer	SE, ET, T	Manual	Moderate	8.3.6	
Ground-Water Fluctuation	SE, ET	Manual	Moderate	8.3.7	8.3

Table A.5 Summary Information on Vadose Zone Water Budget Characterization Methods (Continued)

Technique	Parameters Measured	Manual/ Automatic	S/A/R	Section	Tables
Other Transpiration Methods	T	Manual	Moderate to high ^c	8.3.8	8.3
Thermal Infrared	WE, SE, ET	Either	Low to moderate	1.1.3	1.3
Evapotranspiration (Micrometeorological)					
Empirical Equations	WE, SE, ET, T	Manual	Moderate to high	8.4.1	8.3
Physically Based Equations	WE, SE, ET	Either	Moderate to high	8.4.2	8.3
Mass Transfer Methods	WE, ET, T	Either	Moderate to high	8.4.3	8.3
Energy Budget Methods	WE, SE, ET, T	Either	Moderate to high	8.4.4	8.3
Profile/Gradient Method	WE, SE, ET	Either	Low to moderate	8.4.5	8.3
Eddy Correlation	WE, ET	Either	High	8.4.6	8.3

Note: Boldface = most commonly used methods. Abbreviations for hydrometeorological methods: S = sensitivity = the smallest fraction of a division on a scale on which a reading can be made directly or by estimation; A = accuracy = the closeness with which an observation approaches the true value; R = range of relative humidity that can be measured. Abbreviations for evapotranspiration methods: WE = water evaporation; SE = bare soil evaporation; ET = evapotranspiration; T = transpiration.

^a Recommended accuracy by World Meteorological Organization. Less precise measurements might be acceptable, depending on the purpose of measurements.

^b Range and accuracy of specific thermometers can range considerably; value shown is the recommended specification in U.S. EPA (1987b).

^c For high accuracy, numerous measurements at different locations might be required to adequately characterize the variability of evapotranspiration.

Table A.6 Summary Information on Ground Water Level/Pressure Measurement

Method	Property Measured	Accuracy ^a	Section
Monitoring Well Water Level Measurement			
Steel Tape	Water surface	0.01'	4.1.1
Electric Probe	Water surface	0.02–0.1'	4.1.2
Air Line	Pressure head	0.25'	4.1.3
Pressure Transducers	Pressure head	0.01–0.1'	4.1.4
Popper/Acoustic Probe	Water surface	0.1'	4.1.5
Ultrasonic	Water surface	0.02–0.1'	4.1.6
Mechanical Float	Water surface	0.02–0.5'	4.1.7
Potentiometer Float	Water surface	0.01–0.1' ^b	4.1.7
Electromechanical	Water surface	0.02–0.5'	4.1.8
Flowing Well Head Measurement			
Casing Extensions	Water surface	0.1'	4.1.9
Manometer/Pressure Gauge	Pressure head	0.1–0.5'	4.1.9
Transducers	Pressure head	0.02'	4.1.9
In Situ Piezometers			
	Pressure head	0.02–0.5' ^c	4.1.10

Note: Boldface = most commonly used methods.

^a Water level measurement accuracy in wells taken from Dalton et al. (1991).

^b Reported by Rosenberry (1990) as having accuracy similar to that of pressure transducers.

^c Lower range for measurements with transducers and upper range for pressure gauge.

Table A.7 Summary Information on Aquifer Test Methods

Technique	Confined/ Unconfined	Porous/ Fractured	Aquifer Properties Measured	Section	Table
Shallow Water Table					
Auger Hole	Unconfined	Porous	K (horizontal) ^a	4.2.1	4.5, 7.2
Pit-Baling	Unconfined	Porous ^b	K (undefined)	4.2.1	4.5
Pumped Borehole	Unconfined	Porous	K (undefined)	4.2.1	4.5
Piezometer	Unconfined	Porous	K (undefined)	4.2.2	4.5, 7.2
Tube	Unconfined	Porous ^b	K (vertical)	4.2.2	4.5
Well Point	Unconfined	Porous	K (undefined)	4.2.2	4.5
Two-Hole	Unconfined	Porous	K (undefined)	4.2.3	4.5
Four-Hole	Unconfined	Porous	K (undefined)	4.2.3	4.5, 7.2
Multiple-Hole	Unconfined	Porous	K (undefined)	4.2.3	4.5
Drainage Outflow	Unconfined	Porous	K (undefined)	4.2.3	4.5
Well Tests					
Slug (Injection/Withdrawal)	Both	Porous	K, H, T	4.3.1	4.5
Slug (Displacement)	Both	Porous	K, H, T	4.3.1	4.5
Single-Well Pump	Both	Porous	K, S, T	4.3.2	4.5
Multiple-Well Pump	Both	Porous	A, K, S, T	4.3.2	4.5
Single-Packer	Both	Both	K, H, T	4.3.3	4.5
Two-Packer ^c	Both	Both	K, H, T	4.3.3	4.5
Tracers					
Ions	Both	Both	D, F, V	4.4.1	4.3
Dyes	Unconfined	Both	D, F, V	4.4.2	4.3, 4.6
Gases	Unconfined	Both	D, F, R, V	4.4.3	4.3
Stable Isotopes	Both	Both	D, F, R, V	4.4.4	4.3, 4.6
Radioactive Isotopes	Both	Both	D, F, R, V, T ^d	4.4.5	4.3, 4.6
Water Temperature	Unconfined	Both	D, F, V	4.4.6	4.3
Particulates/Microorganisms	Unconfined	Both	D, F, V	4.4.7	4.3, 4.6
Other Techniques					
Water Balance	Unconfined	Both	R	4.5.1	4.5
Moisture Profile	Unconfined	Porous	S	4.5.2	
Shallow Geothermal	Unconfined	Porous	F, R	1.6.2	
Fluid Conductivity Log	Both	Both	F	3.1.3	
Neutron Activation	Both	Both	F, H, V	3.3.5	
Differential Temperature Log	Both	Both	F	3.5.2	
Flow Meters	Both	Both	F, H, V	3.5.3–3.5.5	
Single-Well Tracer Methods	Both	Both	F, H, V	3.5.6	
Other Borehole Methods	Both	Both	H	Section 3	
Piezometric Map	Both	Both	F, H	4.1	

Note: Boldface = most commonly used methods. A = anisotropy; D = dispersivity; F = flow direction; H = heterogeneity; K = hydraulic conductivity; R = recharge/age; S = specific storage/yield; T = transmissivity; V = velocity.

^a Directional ratings are qualitative in nature. Different references may give different ratings depending on site conditions and criteria used to define directionality. For example, U.S. EPA (1981) and Hendrickx (1990) note that this method often measures primarily horizontal conductivity, whereas Bouma (1983) indicates that the direction is undefined (see Figure 7.2).

^b Can be used in rocky soils; other methods generally require fine-grained soils.

^c Can be used to measure saturated hydraulic conductivity both above and below the water table in open holes in consolidated rock.

^d Actual uses are much more restricted due to health concerns.

Table A.8 Summary Information on Drilling Methods

Drill Method	Casing/ Open-Hole	Fluids Affect Chem.?	Core Samples?	Section Number	Tables
Hollow-Stem Auger	Open Hole	Usually No	Possible	2.1.1	2.2, 2.1.1
Open-Hole Rotary Methods					
Direct Air Rotary with Bit	Open Hole	Yes	Possible	2.1.2	2.2, 2.1.2
Direct Air Rotary with Downhole Hammer	Open Hole	Yes	Possible	2.1.2	2.2, 2.1.2
Direct Mud Rotary	Open Hole	Yes	Possible	2.1.3	2.2, 2.1.3
Reverse Rotary (no casing)	Open Hole	Yes	Possible	2.1.3	2.2
Cable Tool	Either	Usually no	Possible	2.1.4	2.2, 2.1.4
Rotary Drill-Through Methods					
Rotary Casing Driver	Casing	Yes	Possible	2.1.5	2.2, 2.1.5
Dual-Rotary Advancement	Casing	Yes	Possible	2.1.5	
Reverse Circulation Methods					
Reverse Dual-Wall Rotary	Casing	Yes	Possible	2.1.6	2.2, 2.1.6
Reverse Dual-Wall Percussion	Casing	Yes	Possible	2.1.6	
Hydraulic Percussion	Casing	Yes	Possible	2.1.6	2.2
Downhole Casing Advancers	Casing	Yes	Possible	2.1.7	
Jet Percussion	Casing	Possible	Possible	2.1.8	2.2, 2.1.8
Jetting	Open Hole	Possible	No	2.1.8	
Solid-Stem Auger	Open Hole	No	Possible	2.1.9	2.2, 2.1.9
Bucket Auger	Open Hole	No	Possible	2.1.9	
Rotary Diamond	Open Hole	Possible	Yes	2.1.10	
Directional Drilling	Either ^a	Possible	Possible ^b	2.1.11	
Sonic Drilling	Either	Possible	Yes	2.1.12	
Driven Wells	Either	No	No	2.2.1 ^c	2.2
Cone Penetration	Open Hole	No	Possible ^d	2.2.2 ^c	

Note: Boldface = most commonly used methods for monitoring well installation.

^a EC rig uses casing advancement; other methods may involve open-hole advancement.

^b Sampling with a device resembling a split spoon may be possible with some directional rigs.

^c Section includes cross-references to other sections related to method.

^d Geoprobe has developed a core sampler for use with a CPT rig.

Table A.9 Summary of Handheld Soil Sampling Devices

Sampling Device	Applications	Limitations
Spoons and Scoops (Section 2.3.1) ^a	Surface soil samples or the sides of pits or trenches	Limited to relatively shallow depths; disturbed samples
Shovels and Picks (Section 2.3.1)	A wide variety of soil conditions	Limited to relatively shallow depths
Augers^b (Section 2.3.2)		
Screw Auger	Cohesive, soft, or hard soils or residue	Will not retain dry, loose, or granular material
Standard Bucket Auger	General soil or residue	May not retain dry, loose, or granular material
Sand Bucket Auger	Bit designed to retain dry, loose, or granular material (silt, sand, and gravel)	Difficult to advance boring in cohesive soils
Mud Bucket Auger	Bit and bucket designed for wet silt and clay soil or residue	Will not retain dry, loose, or granular material
Dutch Auger	Designed specifically for wet, fibrous, or rooted soils (marshes)	
<i>In Situ</i> Soil Recovery Auger	Collection of soil samples in reusable liners; closed top reduces contamination from caving sidewalls	Similar to standard bucket auger
Stony Soil Auger	Stony soils and asphalt	
Planer Auger	Cleans out and flattens the bottom of predrilled holes	
Posthole/Iwan Auger	Cohesive, soft, or hard soils; readily available	Will not retain loose material
Silage Auger	Silage pits and peat bogs	
Spiral Auger	Used to remove rock from auger holes so that borings can continue with other auger type	
Split Core Auger ^c	Auger with split core for easier recovery of sample; can be used with liner	
Tube Samplers^d (Section 2.3.3)		
Soil Probe	Cohesive, soft soils or residue; representative samples in soft to medium cohesive soils and silts	Sampling depth generally limited to less than 1 m
Thin-Walled Tubes	Cohesive, soft soils or residue; special tips for wet or dry soils available	Similar to Veihmeyer tube
Soil Recovery Probe	Similar to thin-wall tube; cores are collected in reusable liners, minimizing contact with the air	Similar to Veihmeyer tube
Veihmeyer Tube	Cohesive soils or residue to depth of 3 m (maximum of 4.9 m)	Difficult to drive into dense or hard material; will not retain dry, loose, or granular material; may be difficult to pull from ground
Geostick ^c	Spot soil sampling and penetrometer tests	
Peat Sampler	Wet, fibrous, organic soils	

^a Section number in Boulding (1993).

^b Suitable for soils with limited coarse fragments; only the stony soil auger will work well in very gravelly soil.

^c Not included in Boulding (1993).

^d Not suitable for soils with coarse fragments.

Table A.10 Summary of Major Types of Power-Driven Samplers

Tube Type	Applications	Limitations
Disturbed Core Samplers		
<i>Barrel Samplers (Section 2.4.1)^a</i>		
Solid Barrel Sampler	Sand, silts, clays	Disturbed core, questionable recovery and quality below water table
Split Spoon Sampler	Disturbed samples from cohesive soils	Ineffective in cohesionless sands; not suitable for collection of samples for laboratory tests requiring undisturbed soil
<i>Rotating Core (Section 2.4.2)</i>		
Single Tube	Dense unconsolidated and consolidated formations	
Double Tube	Friable, erodible, soluble, or highly fractured formations	
CP Punch Core ^b	Wire line system with various punch shoes; very effective in mixed formations where deep sampling is needed	
Undisturbed Core Samplers		
<i>Thin-Wall Open-Tube Samplers (Section 2.4.3)^a</i>		
Shelby Tube	Undisturbed samples in cohesive soils, silt, and sand above water table	Ineffective in cohesionless sands or stony soil
Continuous Tube/ Laskey Sampler	Same as Shelby tube, except longer barrel designed to operate inside the column of a hollow-stem auger	Same as Shelby tube; no blow counts taken
<i>Thin-Wall Piston Samplers (Section 2.4.4)</i>		
Internal Sleeve Piston Sampler	Collection of sample in heaving sands; used with hollow-stem auger with clamshell bit	Requires use of water or drilling mud for hydrostatic control; only one sample per borehole can be obtained
Fixed-Piston Sampler	Undisturbed samples in cohesive soils, silt, and sand above or below water table	Ineffective in cohesionless sands
Wire Line Piston Sampler	Undisturbed samples in cohesive soils and noncohesive sands; used with clamshell device on hollow-stem auger	In heaving sands only one sample per borehole can be collected because clamshell remains open after sampling
Hydraulic Piston Sampler (Osterberg and Others)	Similar to fixed-piston sampler	Not possible to limit the length of push or to determine amount of partial sampler penetration during push
Stationary Piston Sampler	Undisturbed samples in stiff, cohesive soils; representative samples in soft to medium cohesive soils, silts, and some sands	
Gus Sampler ^b	Similar to stationary piston sampler, except uses hydraulic action	
Free Piston Sampler	Similar to stationary piston sampler	Not suitable for cohesionless soils
Open-Drive Sampler	Similar to stationary piston sampler	Not suitable for cohesionless soils
<i>Specialized Thin-Wall Samplers (Section 2.4.5)</i>		
Pitcher Sampler	Undisturbed samples in hard, brittle, cohesive soils and cemented sands; representative samples in soft to medium cohesive soils, silts, and some sands; variable success with cohesionless soils	Frequently ineffective in cohesionless soils; require use of drilling fluid that may affect quality of sample
Denison Sampler	Undisturbed samples in stiff to hard cohesive soils, cemented sands, and soft rocks; variable success with cohesionless materials	Not suitable for undisturbed sampling of loose, cohesionless soils or soft cohesive soils; requires use of drilling fluid that may affect quality of sample
Vicksburg Sampler	Similar to Shelby tube, but able to sample denser and coarser material	

^a Section number in Boulding (1993).^b Not included in Boulding (1993).

Table A.11 Summary Information on Soil-Solute Monitoring and Sampling Methods

Method	Sampling Method	Depth Limitation	Sections
Indirect Salinity Measurement Methods			
Four-Probe Electrical	Resistivity	Near surface	9.1.1, 1.2.2
Portable EC Probe	Resistivity	1.5 m	9.1.2
<i>In Situ</i> EC Probe	Resistivity	None	9.1.2
Porous Matrix Salinity Sensors	Resistivity	None	9.1.3
Electromagnetic Induction Sensor	Conductivity	2 m	9.1.4, 1.3.1
Dielectric Sensors	Dielectric	2 m ^a	9.1.4, 6.2.3
Time Domain Reflectometry Sensor	Dielectric	Up to 20 m	9.1.4, 6.2.4
Neutron Probe	Nuclear	None	3.3.3, 6.2.2
Direct Soil-Solute Sampling Methods			
Vacuum-Type Porous Cup	Suction	2 m	9.2.1
Vacuum-Pressure Porous Cup	Suction	45 ft	9.2.2
Vacuum High-Pressure Porous Cup	Suction	300 ft	9.2.2
Vacuum-Plate Sampler	Suction	2 m ^a	9.2.3
Membrane Filter	Suction	1–4 m ^b	9.2.4
Hollow Fiber	Suction	2 m ^a	9.2.5
Ceramic Tube Sampler	Suction	2 m ^a	9.2.6
Capillary Wick Sampler	Capillary	^d	9.2.7
BAT Sampler	Suction	45 ft	5.5.2
Trench Lysimeter	Gravity ^c	^d	9.3.1
Caisson Lysimeter	Gravity	3 m+	9.3.1
Pan Lysimeter	Gravity	^d	9.3.1
Glass Block Lysimeter	Gravity	^d	9.3.1
Wicking-Type Sampler	Gravity	^d	9.3.1
Tile Drain Outflow	Gravity	50+ ft	9.3.1
Perched Water Table	Gravity	None	9.3.2
Nylon Sponge	Absorbent	Near surface	9.3.3
Ceramic Rod	Absorbent	Near surface	9.3.3
Solid Soil Water Extraction	^e	None	9.3.4
Soil Saturation Extract	Slurry	None	9.3.5
SEAMIST	Absorbent	100s ft	9.3.7
Methods for Sampling Sensitive Soil Constituents			
Static Soil Gas Sampling	Absorbent	Near Surface	9.4.1
Soil Gas Probes	Suction	^f	9.4.2
Tank Leak Sensors	Various	Typically <2m	9.4.3
Soil Volatiles/Microorganisms	Core	^f	9.3.6

Note: Boldface = most commonly used methods.

^a With vacuum sampling apparatus; greater depths would be possible using vacuum-pressure sampling system.

^b Upper limit would require modification of system to use vacuum-pressure sampling apparatus.

^c Sample is collected by free drainage in all gravity samplers, but suction can be used to bring sample to the surface.

^d Depth limited by the depth to which a hole or trench can be safely dug for installation of sampler in the sidewall; typically 2 m or less.

^e Various methods can be used to extract soil water from a sample: squeezing, displacement, displacement/centrifugation, centrifugation, and adsorption.

^f Depends on density of subsurface material and method of penetration/coring. Soil gas probes used with cone penetration rigs (Sections 2.2.2, 5.5.1, and 5.5.2) can penetrate 100 to 150 ft with favorable soil conditions; greater depths are possible if holes are drilled before insertion of the soil gas probe. Coring depth limits are defined by the type of drilling/coring method used (Sections 2.3 and 2.4).

Table A.12 Summary Information on Ground-Water Sampling Devices

Sampling Device	Max. Sample Depth	Min. Well Diameter	Sample Delivery Rate/Volume ^a	Section	Tables
Portable Positive Displacement Samplers					
Bladder Pumps	1000'	1.5"	0–3.0 gpm	5.1.1	5.2, 5.3
Gear Pumps	200'	2.0"	0–1.5 gpm	5.1.2	5.2, 5.3
Helical Rotor Pumps	160'	2.0"	0–1.5 gpm	5.1.3	5.2, 5.3
Gas-Drive/Displacement	300'	1.0"	0.1–10 gpm	5.1.4	5.2, 5.3
Gas-Drive Piston Pumps	900'	1.5"	0–1.5 gpm	5.1.5	5.2, 5.3
Mechanical Piston Pumps	Variable	1.0–4.0"	Variable	5.1.6	
Other Portable Ground-Water Sampling Pumps					
Peristaltic Suction Lift	25'	0.5"	0.01–8 gpm	5.2.1	5.2, 5.3
Centrifugal Suction Lift	15'	1.0"	1.0–25 gpm	5.2.1	
Variable-Speed Submersible Centrifugal Pump	290'	1.75"	0.026–8 gpm	5.2.2	5.2, 5.3
Other Submersible Centrifugal Pumps	2000'	4.0+"	5.0–60 gpm	5.2.2	5.2, 5.3
Inertial-Lift Pump	200'	1.5"	0–2.0 gpm	5.2.3	
Gas-Lift Pump	Variable	1.0"	Variable	5.2.4	5.2
Jet (Venturi) Pump	200'	<1.0"	25–30 gpm	5.2.5	
Packer Pumps ^b	Variable	2.0"	Variable	5.2.6	
Portable Grab- and Depth-Specific Samplers					
Open Bailer^c	No limit	0.5"	Variable	5.3.1	5.2, 5.3
Point-Source Bailer^c	No limit	0.5"	Variable	5.3.1	5.2, 5.3
Syringe Sampler	No limit	1.5"	0.01–0.2 gal	5.3.2	5.2, 5.3
Westbay Sampler	No limit	1.5"	40 ml	5.3.2	
Kemmerer/Van Dorn	No limit	1.0"	Variable	5.3.3	
Coliwasa	5'	2.0"	Variable	5.3.3	
Stratified Sample Thief	No limit	1.5"	Variable	5.3.3	
Swabbing	No limit	6.0"	Variable	5.3.3	
Portable/Permanent <i>In Situ</i> Samplers/Sensors					
Hydropunch	150' ^d	NA	500–1250 ml	5.5.1	
BAT Sampler	100' ^d	NA	150 ml	5.5.2	
Other CPT Samplers ^e	25'	NA	0.01–0.3 gpm	5.5.2	
Other <i>In Situ</i> Probes ^e	25'	NA	0.01–0.3 gpm	5.5.3	
Eh, pH Probes	No limit	1.0"	NA	5.5.4	
Ion-Selective Electrodes	No limit	1.0"	NA	5.5.5	
Fiber-Optic Sensors	No limit	±2.0"	NA	5.5.6	
Other Chemical Sensors	No limit	2.0–6.0"	NA	10.6.5	

Note: Information is for general guidance only. Boldface = most commonly used devices.

^a Sample delivery rates and volumes are averages based on typical field conditions. Actual rates are a function of diameter of monitoring well installation, size and capacity of sampling device, hydrogeologic conditions, and depth to sampling point.

^b Depends on type of pump used (submersible, gas lift, suction) — see appropriate device for ratings.

^c Not recommended for use with sensitive chemical constituents (see text discussion).

^d Unlimited depth if hole is bored to desired depth before using sampler. Otherwise, actual depth of penetration is highly dependent on type of soil material.

^e Depth and pumping rate depends on type of suction-lift device used. Values shown are for peristaltic pump.

Table A.13 Summary Information on Sample Processing/Analytical Techniques

Technique/Instrumentation	Technology Status ^a	Sample Matrix ^b	Contaminant Type ^c	Detection Limit ^d	Section/Table
Chemical Field Measurement Techniques/Sensors					
pH/Alkalinity/Acidity	I/CP	W, S	—	—	10.1.1, 5.5.4
Eh	I/CP	W, S	—	—	10.1.2, 5.5.4
Dissolved Oxygen	I/CP	W	—	ppm	10.1.2, 5.5.4
Temperature	I/CP	W	—	—	10.1.3
Electrical Conductance	I/CP	W, S	—	—	10.1.3
Filterable Residue	I/CM	W	—	—	10.1.3
Other Specific Ion Electrodes	II/CP	W	EA	ppm	5.5.5
Solid/Porous Fiber Optic	IV	W, S, A	VOC	ppm	5.5.6
Immunochemical Fiber Optic	IV	W, S, A	SVO	ppb-ppm	5.5.6, 10.5.2
Electrochemical Sensors	IV	W, A	VOC, TG	ppb-ppm	10.6.5
SAW Probes	IV	A	VOC, TG	ppm	10.6.5
Piezoelectric Sensors	IV	A	VOC	ppm	10.6.5
Semiconductor Sensors	IV	A, W	VOC	ppm-%	10.6.5
Sample Extraction Procedures					
Headspace Analysis	I	A	VOC	—	10.2.1
Vacuum Extraction	I/CP	A	VOC	—	10.2.1
Purge and Trap	I/CP	W	VOC	—	10.2.2
Solvent Extraction	I/CP	S	SVO, VOC	—	10.2.3
Thermal Digestion	II/CP	W, S	EA, HM	—	10.2.4
Thermal Extraction	II/CP	W, S	SVO	—	10.2.4
Thermal Desorption	III/CP	W, S	VOC, SVO	—	10.2.4
Supercritical Fluid Extract	III/CP	W, S	VOC, SVO	—	10.2.5
Membrane Extraction	IV	W	VOC	—	10.2.5
Sorbent Extraction	I/CP	A, W	VOC, SVO	—	10.2.5
Gaseous Phase Analytical Techniques					
Photo Ionization Detector	I/CP	A	VOC	ppb-ppm	10.3.1
Flame Ionization Detector	I/CP	A	VOC	ppb-ppm	10.3.1
Argon Ionization Detector	III/CP	A	VOC	100s ppb-ppm	10.3.1
Explosimeter	I/CP	A	VOC	%	10.3.2
Catalytic Surface Oxidation	I/CP	A	VOC, TG	ppm-%	10.3.2

Table A.13 Summary Information on Sample Processing/Analytical Techniques (Continued)

Technique/Instrumentation	Technology Status ^a	Sample Matrix ^b	Contaminant Type ^c	Detection Limit ^d	Section/Table
Detector Tubes	I/CP	A	VOC, TG	high ppm	10.3.2
Gas Chromatography (GC)	II/CP, CM	A, W	VOC, SVO, TR	ppb-ppm	10.3.3/Table 10.3
Mass Spectrometry (MS)	II/CF, CM	A	VOC, SVO, TR	ppm	10.3.4/Table 10.3
GC/MS	II/CM	A	VOC, SVO, TR	ppb	10.3.4/Table 10.3
Ion Trap MS	IV	A	VOC, SVO	ppb-ppm	10.3.4
AA Spectrometry	II/CM	A, W	EA, HM	ppb-ppm	10.3.5/Table 10.3
ICP-AES	II	A, W	EA, HM	ppb-ppm	10.3.6/Table 10.3
Ion Mobility Spectrometer	II/CP	A	VOC, SVO, TG	ppt-ppm	10.3.7
Luminescence/Spectroscopic Techniques					
X-Ray Fluorescence	II/CP, CM	S, W	HM	10s–100s ppm	10.4.1
UV Fluorescence	II	S, W	VOC	sub-ppm	10.4.2/Tables 10.3,10.4.2
Room Temperature Phosphorimetry	III	S, W	VOC, SVO	ppb-ppm	10.4.2/Table 10.4.2
Synchronous Luminescence	III	W	VOC, SVO	ppm	10.4.2
Synchronous Fluorescence	III	W	VOC, SVO	ppm	10.4.2/Table 10.4.2
UV-Visible Spectrophotometry	III	A, W	VOC	ppb-ppm	10.4.3/Tables 10.3,10.4.3
Infrared Spectroscopy	II	A, W, S	M, VOC, SVO	ppm–1000s ppm	10.4.3/Tables 10.3,10.4.3
FTIR Spectroscopy	II/CP, CM	A	VOC	ppb-%	10.4.4/Table 10.4.4
Scattering/Absorption Lidar	IV	A	VOC	ppm	10.4.4
Raman Spectroscopy/SERS	II	W, S	VOC, SVO	ppb-ppm	10.4.4/Table 10.4.4
Near IR Reflectance/Trans. Spect.	IV	S	VOC	100s–1000s ppm	10.4.4/Table 10.4.4
Wet Chemistry					
Chemical Colorimetric Kits	II/CP	W	EA, HM, SVO	ppb–100s ppm	10.5.1/Table 10.3
Other Colorimetric Methods	I/CP	W	TR	ppb–100s ppm	10.5.1/Table 10.3
Titrimetry	I/CP	W	EA, HM, TR	ppb–100s ppm	10.5.1
Immunoassay Colorimetric Kits	II/CP	W	SVO	ppb-ppm	10.5.2
Ion Chromatography	II	W	EA	ppm–100s ppm	10.5.3/Table 10.3
High-Pressure Liquid Chromatography	II/CM	W	SVO, TR	ppb-ppm	10.5.3/Table 10.3
Thin-Layer Chromatography	II	W	SVO	ppm	10.5.3
Coulometry	II	W	EA, TR	ppb-ppm	10.5.4
Polarography	II	W	EA	sub-100s ppm	10.5.4
Stripping Voltammetry	II	W	EA	ppt-ppm	10.5.4

Radiological					
Neutron Activation/INNA	II	S, W	EA, TR	10s ppm	10.6.1, 3.3.5, 3.3.6
PIXE	II	S, W	EA, HM	10s–100s ppm	10.6.1/Table 10.3
Radiation Detectors	I/CP	A, S, W	R, TR	Varies	10.6.1, 3.3.1
X-Ray Diffraction	II	S	M	—	10.6.1
Gamma Spectrometry	I/CP	S	M	—	3.3.2
Other					
Gravimetric	I/CP	W, S	P, TDS	%	10.6.2
Volumetric	I/CP	S, W, A	P	—	10.6.2
Nuclear Magnetic Resonance	I/CP	S, W	M, P	—	10.6.3, 3.2.4
Magnetic Susceptibility	II	S	M	—	10.6.3
Electron Spin Resonance	II	S, W, A	M	—	10.6.3
Optical Microscope	II/CP	S	M, P	—	10.6.4
Scanning Electron Microscope	II	S	M	—	10.6.4
Electron Microprobe	II	S	M	High ppm	10.6.4
Field Bioassessment	II	—	VOC, HM	—	10.6.6
Toxicity Tests	II	W, S, A	VOC, SVO, HM	—	10.6.6
Biomarkers	III	W, S, A	VOC, SVO, HM	—	10.6.6

Note: Boldface = most commonly used/proven field techniques.

^a I = well-established and routinely used field technology; II = well-established laboratory technology for which experience in field applications is moderate to limited; III = relatively well-established technology for which there is limited field experience; IV = developing technology with potentially useful field applications; CP = commercially available portable instruments; CF = commercially available fieldable instruments; CM = commercial/custom mobile laboratories available.

^b A = air–gaseous matrix; S = soil–solid matrix; W = water–aqueous–liquid matrix. Volatile and semivolatiles in water and solid samples can be extracted for analysis by gaseous phase analytical techniques. Similarly, analytes can be extracted from solids samples for analysis using wet chemistry techniques.

^c EA = elemental/ionic analysis; HM = metals; M = mineralogy; P = physical characterization; R = radioisotopes; SVO = semivolatile organics; TG = toxic gases; TDS = total dissolved solids; TR = tracer studies; VOC = volatile organic compounds.

^d Ranges for specific instruments and analytes might differ from range shown by orders of magnitude. In general, detection limits for soils will be higher than those for ground water.

Table A.14 ASTM Standard Methods Cited in This Handbook

ID #/Year ^a	Title ^b
D1452-80	Practice for Soil Investigation and Sampling by Auger Borings
D1586-84	Method for Penetration Test and Split-Barrel Sampling of Soils
D1587-83	Practice for Thin-Walled Tube Sampling of Soils
D2113-83	Practice for Diamond Core Drilling for Site Investigation
D2434-68	Test Method for Permeability of Granular Soils (Constant Head)
D2488-93	Practice for Description and Identification of Soils (Visual-Manual Procedures)
D3550-84	Practice for Ring-Lined Barrel Sampling of Soils
D4043-91	Guide for Selection of Aquifer-Test Field and Analytical Procedures in Determination of Hydraulic Properties by Well Techniques
D4210-89	Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting of Low-Level Data (Vol. 11.01)
D4404-84	Test Method for Determination of Pore Volumes and Pore Volume Distribution of Soil and Rock by Mercury Intrusion Porosimetry
D4696-92	Guide for Pore-Liquid Sampling from the Vadose Zone
D4700-91	Guide for Soil Sampling from the Vadose Zone
D5084-90	Method for Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter
D5088-90	Practice for Decontamination of Field Equipment Used at Nonradioactive Waste Sites
D5092-90	Recommended Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers
D5126-90	Guide for Comparison of Field Methods for Determining Hydraulic Conductivity in the Vadose Zone
D5299-92	Guide for the Decommissioning of Ground Water Wells, Vadose Zone Monitoring Devices, Boreholes and Other Devices for Environmental Activities
D5314-92	Guide for Soil Gas Monitoring in the Vadose Zone
D5387-93	Guide for Elements of a Complete Data Set for Non-Cohesive Sediments (Vol. 11.02)
D5447-93	Guide for Application of a Ground-Water Flow Model to a Site Specific Problem
D5518-94	Guide for Acquisition of Aerial Photography and Imagery for Establishing Historic Site-Use and Surficial Conditions
D5730-01	Guide for Site Characterization for Environmental Purposes with Emphasis on Soil, Rock, the Vadose Zone and Ground Water
D5903-96	Guide for Planning and Preparing for a Ground Water Sampling Event
D6169-98	Guide for Selection of Soil and Rock Sampling Devices Used with Drill Rigs for Environmental Investigations
D6187-97	Practice for Cone Penetrometer Technology Characterization of Petroleum Contaminated Sites with Nitrogen Laser-Induced Fluorescence
D6235-98a	Practice for Expedited Site Characterization of Vadose Zone and Ground Water Contamination at Hazardous Waste Contaminated Sites
D6452-99	Guide for Purging Methods for Wells Used for Ground-Water Quality Investigations
D6517-00	Guide for Field Preservation of Ground-Water Samples
D6527-00	Test Method for Determining Unsaturated and Saturated Hydraulic Conductivity in Porous Media by Steady-State Centrifugation
D6539-00	Test Method for Measurement of Pneumatic Permeability of Partially Saturated Porous Materials by Flowing Air
D6564-00	Guide for Field Filtration of Ground-Water Samples
D6705-01	Practice for Direct Push Installation of Pre-Packed Screen Monitoring Wells in Unconsolidated Aquifers
E1912-98	Guide for Accelerated Site Characterization at Confirmed or Suspected Petroleum Releases

^a Last two digits indicate the year in which the standard was approved or the last year in which substantive revisions were made to the standard.

^b In Vols. 4.08 (Soil and Rock I: D420 to D4914) and 4.09 (Soil and Rock II: D4943 to latest; Geosynthetics), unless otherwise indicated. Volumes and individual standards can be purchased from ASTM, 1916 Race St., Philadelphia, PA 19103-1187 (215-299-5585).

Appendix A References

- Adams, W.M., S.W. Wheatcraft, and J.W. Hess. 1983. Downhole Sensing Equipment for Hazardous Waste Site Investigations. In: Proceedings of the 4th National Conference on Management of Uncontrolled Hazardous Waste Sites, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 108–113.
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- Rosenberry, D.O. 1990. Effect of Sensor Error on Interpretation of Long-Term Water-Level Data. *Ground Water* 28:927–936. [Pressure transducer, potentiometer float]
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- Thornhill, J.T. and B.G. Benefield. 1990. Injection-Well Mechanical Integrity. EPA/625/9-89/007. Available from CERL.*
- U.S. Environmental Protection Agency (EPA). 1981. Process Design Manual for Land Treatment of Municipal Wastewater. EPA/625/1-81/013. [U.S. Army Corps of Engineers, U.S. Department of the Interior, and U.S. Department of Agriculture are also authors of this report]
- U.S. Environmental Protection Agency (EPA). 1987a. A Compendium of Superfund Field Operations Methods, Part 2. EPA/540/P-87/001 (OSWER Directive 9355.0-14, NTIS PB88-181557), 644 pp.
- U.S. Environmental Protection Agency (EPA). 1987b. On-Site Meteorological Program Guidance for Regulatory Modeling Applications. EPA/450/4-87/013 (NTIS PB87-227542), 187 pp.
- Wheatcraft, S.W., K.C. Taylor, J.W. Hess, and T.M. Morris. 1986. Borehole Sensing Methods for Ground-Water Investigations at Hazardous Waste Sites. EPA/600/2-86/111 (NTIS PB87-132783).

* See Preface for information on how to obtain documents.

Index to ASTM Field and Laboratory Methods Possibly Pertinent to Environmental Site Characterization

Table A.14 contains a consolidated list of all standard methods developed by the American Society for Testing and Materials (ASTM) that are mentioned in this handbook. This appendix lists and provides an index for more than 520 potential field and laboratory methods for sampling and characterization of soil, ground water, and waste materials. Other ASTM methods for measuring site parameters that may need to be monitored during environmental site investigations, such as humidity and wind, are also included. All standards listed in [Table B.1](#) follow in alphanumeric sequence. The appendix updates ASTM D5730-02 (Guide to Site Characterization for Environmental Purposes) to include 23 additional standards. Any later editions of that standard should be referred to for the most up-to-date list of possibly relevant ASTM standards.

Most ASTM standards relevant to investigation of soil and ground water have been developed by Committee D18 on Soil and Rock. Prior to 1994, all Committee D18 standards were published in Volume 4.08 of ASTM's annual books of standards. Beginning in 1994, a second volume, Volume 4.09, was added. For a specific standard, a volume published prior to the current year can be used, provided its year of issuance is later than the most recent revision to the standard. For example, ASTM D1452-80 could be used from any book of standards published since 1981 (note that there is usually about a year's lag time from approval of a standard or revision to its publication in the full book of standards). If you are uncertain whether a version of a standard you have is current, contact ASTM to make sure: 100 Barr Harbor Dr., West Conshohocken, PA 19428; 610-832-9585; <www.astm.org>.

The following ASTM compilations may be useful for environmental site characterization:

ASTM Standards on Ground Water and Vadose Zone Investigations: Drilling, Sampling, Geophysical Logging, Well Installation and Decommissioning, 2nd ed. 1999, 561 pp. [56 standards]

ASTM Standards Related to Phase II Environmental Site Assessment Process. 1998, 333 pp. [22 standards]

ASTM Standards on Environmental Site Assessments for Commercial Real Estate, 2nd ed. 1994, 55 pp. [Includes E1527 and E1528]

ASTM Standards on Environmental Sampling, 2nd ed. 1997, 1008 pp. [138 standards]

ASTM Standards on Determining Subsurface Hydraulic Properties and Ground Water Modeling, 2nd ed. 1999, 350 pp. [45 standards]

ASTM Standards on Design, Planning and Reporting of Ground Water and Vadose Zone Investigations, 2nd ed. 1999, 600 pp. [44 standards]

ASTM Standards Related to Environmental Site Characterization, 2nd ed. 2002, 2078 pp. [162 standards]

Table B.1 Index to ASTM Field and Laboratory Methods Possibly Pertinent to Environmental Site Characterization

Topic	ASTM Standard
General	
Reports	Indexing papers and reports (<i>D3584</i>); use of modernized metric system (<i>E380</i>)
Terminology	Soil, rock, and contained fluids (<i>D653</i>); atmospheric sampling (<i>D1356</i>); basic statistics (<i>D4375</i>); waste and waste management (<i>D5681</i>); water (<i>D1129</i>)
Objective-Oriented Guides	Acquisition of file aerial photography and imagery for establishing historic site use and surficial conditions (<i>D5518</i>); <u>Contaminated Sites</u> : Expedited site characterization (<i>PS85</i> , <i>D6235</i>); developing conceptual site models for contaminated sites (<i>E1689</i>); accelerated site characterization for petroleum releases (<i>E1912</i> , <i>PS3</i>); <u>Remediation/Corrective Action</u> : Risk-based corrective action (<i>E2081</i> , <i>E2247</i> — protection of ecological resources, <i>PS104</i>); corrective action at petroleum release sites (<i>E1599</i> , <i>E1739/ES38</i> — risk based); short-term measures or early actions for site remediation (<i>D5745</i>); natural attenuation (<i>E1943</i>); brownfields (<i>E1948</i>); cleanup levels (<i>D6597</i>); activity and use limitations (<i>E2091</i>); <u>Real Estate/Property Assessments</u> : Environmental condition of property area types for defense base closure (<i>D5746</i>); environmental baseline surveys (<i>D6008</i>); baseline property condition assessments (<i>E2018</i>); real estate property transactions (Phase I: <i>E1527</i> , <i>E1528</i> , <i>E2247</i> — forestland/rural; Phase II: <i>E1903</i>); <u>Site Characterization</u> : Environmental (<i>D5730</i> — this guide, <i>D5995</i> — cold regions; <i>D6067</i> — ECPT); engineering and construction purposes (<i>D420</i>); <u>Septic System Characterization</u> : Surface (<i>D5879</i>); subsurface (<i>D5921</i>); sizing (<i>D5925</i>); <u>Environmental Management</u> : Development and implementation of a pollution prevention program (<i>E1609</i>); building life cycle assessment (<i>E1991</i>); life cycle costing for pollution prevention (<i>PS14</i>); UST Operational Conformance (<i>E1990</i>); assessment of buried steel tanks (<i>ES40</i>); environmental liability disclosure (<i>E2173</i>); environmental regulatory compliance audits (<i>E2107</i> , <i>PS11</i>); estimating environmental monetary costs and liabilities (<i>E2137</i>); evaluation of an organization's environmental management system (<i>PS12</i>); development and implementation of a source reduction program (<i>PS26</i>)
Certification/Accreditation	Environmental professionals (<i>E1929</i>); personnel engaged in testing soil and rock (<i>D5255</i>)
Sampling	
General	Collection and preservation of information and physical items by a technical investigator (<i>E1188</i>); probability sampling of materials (<i>E105</i>); <u>Sampling Design</u> : Waste management sampling design optimization (<i>D6311</i>); ranked set sampling (<i>D6582</i>)
Air	Choosing locations and sampling methods for atmospheric deposition at nonurban locations (<i>D5111</i> , <i>D5012</i>); guide for laboratories (<i>D3614</i>); diffusive samplers (<i>D6246</i>); flow rate calibration of personal sampling pumps (<i>D5337</i>); planning ambient air sampling (<i>D1357</i>); ambient air analyzer procedures (<i>D3249</i>); sampling stationary source emissions (<i>D5835</i>); <u>Airborne Microorganisms</u> : Sampling at municipal solid waste facilities (<i>E884</i>); <u>Aerosols</u> : <i>D6552</i> ; <i>D6061</i> ; <i>D6062M</i> ; <u>Sampling Organic Vapors/Toxic Vapors</u> : Method selection (<i>D6345</i>) ; charcoal tube absorption (<i>D3686</i>); canister (<i>D5466</i>); detector tubes (<i>D4490</i>); length-of-stain dosimeter (<i>D4599</i>); sorbent selection (<i>D6196</i>); PAHs (<i>D6209</i>); FTIR (<i>D6348</i>); <u>Particulate Matter Determination</u> : Filter absorbance method (<i>D1704</i> , <i>D1704M</i>); high-volume sampler (<i>D4096</i> , <i>D4536</i>); stationary source (<i>DD6331</i>); dustfall (<i>D1739</i> — settleable particulates); <u>Worker Protection</u> : Air monitoring at waste management facilities for worker protection (<i>D4844</i>); air sampling strategies for worker and workplace protection (<i>E1370</i>); collection of airborne particulate lead during abatement and construction activities (<i>E1553</i>); activated charcoal samplers (<i>D4597</i>); liquid sorbent diffusional samplers (<i>D4598</i>); pesticides and PCBs (<i>D4861</i>); sampling indoor air quality of building (<i>D5791</i>)
Biological Materials	Aseptic sampling (<i>E1287</i>)

Table B.1 Index to ASTM Field and Laboratory Methods Possibly Pertinent to Environmental Site Characterization (*Continued*)

Topic	ASTM Standard
Soil/Rock/Sediments	Minimum set of data elements for soil sampling (D5911); locational data elements (D6168); format for exchange of computerized rock and soil data (D6453); selection of soil and rock sampling devices used with drill rigs (D6169); direct-push soil sampling (D6282); <u>Drilling Methods</u>: Selection of drilling methods (D6286) ; cable tool (D5875); casing advancement (D5872); diamond core drilling (D2113); direct air rotary (D5782); direct fluid rotary (D5783); direct rotary wire line (D5876); dual-wall reverse circulation (D5781); hollow-stem auger (D5784, D6151); <u>Field Sampling and Handling Methods</u> : Auger sampling (D1452); radionuclides (C998); core barrel samplers (D6640); ring-lined barrel (D3550); split barrel (D1586); thin-wall tube (D1587); piston sampler (D6519); volatile organics (D4547, D6418 — En Core sampler); hollow-stem auger (D6151); coring/logging cement and lime stabilized soils (D6236); <u>Sediments</u> : fluvial sediment in motion (D4411, D6236 — transit ratios/sampling depth); submerged (D4823); monitoring sediments in watershed (D6145); handling storing and preparing soft undisturbed marine soil (D3213); collection for toxicological testing (E1391)
Vadose Zone	<u>Field Methods</u> : Pore liquids (D4696); soil (D4700) ; soil gas (D5314)
Water	Reporting water analysis results (D596); reporting water chemical analyses (D6568); purgeable headspace sampling (D3871); waterborne oils (D4489); continual on-line monitoring (D3864); on-line measurement of pH (D6569); on-line measurement of turbidity (D6699); filterable and nonfilterable matter (D5907); on-line sampling/analysis (D5540 — flow and temperature control); water-formed deposits (D887); <u>Planning</u> : Water quality measurement program (D5612); water monitoring programs (D5851); <u>Ground Water</u> : Sampling methods (D4448); selection of sampling and purging devices (D6634) ; direct-push sampling (D6001); planning a ground-water sampling event (D5903); documenting a ground-water sampling event (D6089); bailers (D6699); purging methods (D6452, D6771 — low-flow purging and sampling); field filtration (D6564); field sample preservation (D6517); <u>Surface Water</u> : Dipper or pond sampler (D5358); monitoring aqueous nutrients in watersheds (D6146); collection of water quality parameters from open channels (D6764); <u>Closed Conduits</u> : Equipment (D1192); sampling (D3370); <u>Laboratory Practices</u> : D3856
Waste/Contaminants	<u>General Guidance</u> : General planning (D4687); sampling equipment selection (D6232) ; representative sampling (D6044); composite sampling and field subsampling (D6051); heterogeneous wastes (D5956); laboratory subsampling (D6323); <u>Specific Sampling Procedures</u> : Bailers (D6699); bituminous materials (D140); COLIVASA (D5495); drums (D6063 — general, D5679 — consolidated solids, D5680 — unconsolidated solids, D5743 — single or multilayered liquids); pipes and other point discharges (D5013); grab and discrete depth samplers (D6759); scoop (D5633); trier sampler (D5451); unconsolidated waste from trucks (D5658); UST release detection devices (<i>E1430</i> , <i>E1526</i>); volatile organics (D4547); waterborne oils (D4489); oil–water mixtures for oil spill recovery equipment (F1084); waste piles (D6009); wastewater automatic samplers (D538); wipe sampling (D6601)
Preservation/Transport	Sample chain of custody (D4840); estimation of holding time for water samples (D4515, 4841); <u>Field Methods</u> : Rock core samples (D5079); sample containers for organic constituents (D3694); soil samples (D4220); sediments for toxicological testing (E1391); preservation/preparation of waterborne oil samples (D3325, D3326); handling, storing, and preparing soft undisturbed marine soil (D3213)
Decontamination of Field Equipment	<u>Field Methods</u> : Nonradioactive waste sites (D5088); low-level radioactive waste sites (D5608)
Data Management/Analysis	<u>QA/QC</u> : Waste management environmental data (D5283); waste management DQOs (D5792); precision and bias (E177); QC specification for organic constituents (D5789); <u>Data Analysis</u> : Evaluation of technical data (E678); outlying observations (E178); reporting results of examination and analysis of water-formed deposits (D933); <u>Waste Management Data</u> : Data assessment (D6333); decision point (D6250); <u>Geostatistics</u> : Reporting geostatistical site investigations (D5549); analysis of spatial variation (D5922); selection of kriging methods (D5923); selection of simulation approaches (D5924); <u>Spatial Data</u> : Digital geospatial metadata (D5714); see also ground water (data analysis)

Table B.1 Index to ASTM Field and Laboratory Methods Possibly Pertinent to Environmental Site Characterization (*Continued*)

Topic	ASTM Standard
Soil/Rock Hydrologic Properties	
Infiltration Rate	<u>Field Methods</u> : Double-ring infiltrometer (D3385); sealed double-ring infiltrometer (D5093)
Matric Potential	<u>Field Methods</u> : Tensiometers (D3404); <u>Laboratory Method</u> : Filter paper method (D5298)
Water Content	<u>Field Methods</u> : Calcium carbide method (D4944); neutron probe (D3017 — shallow depth, D5220 — depth probe; D6031 — horizontal, slanted, and vertical access tubes); time domain reflectometry (D6565, D6780); <u>Laboratory Methods</u> : Direct heating method (D4959); microwave oven method (D4643); standard oven drying method (D2216); centrifuge moisture equivalent (D425)
Hydraulic Conductivity	<u>Field Methods</u> : Vadose zone (D5126) ; <u>Laboratory Methods</u> : Granular soils (D2434 — $>1 \times 10^{-3}$ cm/sec); low permeability soils (D5084 — $<1 \times 10^{-3}$ cm/sec); rigid-wall compaction-mold permeameter (D5856); effect of freeze-thaw (D6035); peat (D4511); unsaturated/saturated with centrifugation (D6527); partially saturated (D6539); see also ground water/aquifer hydraulic properties
Other Hydrologic Properties	Soil water moisture flux (D6642); <u>Laboratory Methods</u> : Air permeability (D4525); Soil water retention (D2325 — medium/coarse textured, D3152 — fine textured, D6836)
Soil/Rock/Sediment Physical Properties	
Particle Size	<u>Soil Laboratory Methods</u> : Analysis (D422); dry preparation (D421); <200 sieve (D1140); wet preparation (D2217); <u>Sediment</u> : Selection of methods for fluvial sediment (D4822)
Pore Volume/Specific Density	<u>Laboratory Methods</u> : Pore volume (D4404); specific gravity (D854, D5550 — gas pycnometer)
Soil Density	<u>Field Methods</u> : Drive cylinder (D2937); gamma-gamma (D2922 — <12 in., D5195 — >12 in.); peat (D4531); penetration (D1586); rubber balloon method (D2167), sand-cone method (D1556); sand replacement method (D4914); sleeve method (D4564); time domain reflectometry (D6780); water replacement method (D5030); nuclear method (D6031)
Cone Penetration	<u>Field Methods</u> : <i>In situ</i> cone penetration testing (D3441, D5778); CPT stress wave energy measurements (<i>D4633</i>); liquefaction potential evaluation (D6066); ECPT for environmental site characterization (D6067); LIF characterization of petroleum contamination (D6187)
Classification	<u>Field Methods</u> : Field logging (D5434); noncohesive sediments (D5387); peat (D4544 — deposit thickness, degree of humification — D5715); sediments (D4410); visual-manual procedure (D2488 — unified, D4083 — frozen soils); rock mass classification (D5878); rock quality designation (D6032); <u>Laboratory Methods</u> : frozen soils (D4083); natural mineral aggregates (C294); peat (D2607); unified soil classification (D2487)
Geophysical Properties	<u>Surface Geophysical Methods</u> : Selecting surface geophysical methods (<i>PS78, D6429</i>) ; seismic refraction (D5777); soil resistivity (Wenner four-electrode method — G57); DC resistivity (D6431); GPR (D6432); electromagnetic (D6639 — frequency domain, D6820 — time domain), gravity (D6430); <u>Borehole Geophysical Methods</u> : Crosshole seismic testing (D4428/D4428M); planning and conducting borehole geophysical logging (<i>D5753</i>) ; mechanical caliper (D6167); electromagnetic induction (D6726), gamma (D6274), neutron (D6727)

Table B.1 Index to ASTM Field and Laboratory Methods Possibly Pertinent to Environmental Site Characterization (*Continued*)

Topic	ASTM Standard
Engineering Properties	<u><i>In Situ Field Methods</i></u> : Bearing capacity/ratio (D1194, D4429); deformability and strength of weak rock (D4555); direct shear strength (D4554, D5607); erodibility (D5852); frost heave/thaw susceptibility (D5918); extensometers (D4403); <i>in situ</i> creep (D4553); <i>in situ</i> modulus of deformation (D4394 — rigid plate, D4395 — flexible plate, D4506 — radial jacking test, D4729 — flatjack method, D4791 — borehole jack); <i>in situ</i> stress (D4623 — borehole deformation gauge, D4645 — hydraulic fracturing, D4729 — flatjack method); pressure measurement (D4719 — pressure meter, D5720 — transducer calibration); stiffness (D6758); vane shear test (D2573); <u><i>Laboratory Methods</i></u> : California bearing ratio (D1883); classification (D2487); compaction (D698, D1557, D5080); compressive strength (D2166, D2938); consolidation (D2435); core dimensional and shape tolerances (D4543); dispersive characteristics (D4221 — double hydrometer, D4647 — pinhole test, D6572 — crumb test); elastic properties (D2845, D3148); impact value (D5874); linear displacement (D6027 — calibrating transducers); liquid limit (D4318); moisture content penetration resistance (D1558); one-dimensional swell (D4546); plastic limit/plasticity index (D4318); point load strength (D5731); rock hardness (D5873); shrinkage factors (D427, D4943); tensile strength (D2936, D3967); thermal properties (D5334, D5335); triaxial compression (D2850, D2664, D4406, D4767, D5311, D5407); uniaxial compression (D4341, D4405); use of significant digits (D6026); shear tests (D4648 — vane, D6467 — drained, D6528 — undrained); <u><i>Evaluation of Laboratories</i></u> : D3740
Miscellaneous	<u><i>Field</i></u> : Geotechnical mapping of large underground openings in rock (D4543); <u><i>Laboratory Methods</i></u> : X-ray radiography (D4452)
Peat/Organic Soils	<u><i>Laboratory Methods</i></u> : Bulk density (D4531); classification (D2607); hydraulic conductivity (D4511); pH (D2976); moisture/ash/organic matter (D2974)
Frozen Soils	<u><i>Field</i></u> : Description (D4083); <u><i>Laboratory</i></u> : Creep properties by uniaxial compression (D5520)
Soil/Rock/Sediment Chemistry	
Basic Chemistry	<u><i>Field Methods</i></u> : Soil pH for corrosion testing (G51); <u><i>Laboratory Methods</i></u> : Calcium carbonate (D4373); pH (D4972); soluble salt content (D4542); diagnostic soil test for plant growth and food chain protection (D5435); minimum requirements for laboratories engaged in chemical analysis (D5522)
Soil Contaminants	Nitroaromatic and nitramine explosives (D5143); screening fuels (D5831); PCBs using room temperature phosphorescence (<i>PS47</i>); radionuclides (C998, C999); petroleum contamination with CPT/LIF (D6187)
Sediments	Preparation for chemical analysis (D3975, D3976)
Ground Water	
Characterization/ Monitoring	Assessing aquifer sensitivity and vulnerability (D6030); conceptualization and characterization (D5979); wetland functions (E1938); existing wells (D5980); locating abandoned wells (D6285); monitoring karst and fractured rock aquifers (D5717); statistical approaches for ground-water detection monitoring programs (<i>PS64</i> , D6312); nomenclature for aquifers (D6106)
Data Elements	<u><i>Field Methods</i></u> : Minimum set (D5254); additional identification descriptors (D5408); additional physical descriptors (D5409); additional usage description (D5410); selection of data elements (D5474)
Data Analysis/ Presentation	Presentation of water level information (D6000); <u><i>Chemical Analysis</i></u> : Diagrams for single analyses (D5738); trilinear diagrams (D5754); diagrams based on data analytical calculations (D5877); use of maps (D6036)
Monitoring Wells	<u><i>Field Methods</i></u> : Design/installation (D5092) ; protection (D5787); direct push (D6724, D6725 — prepacked screens); decommissioning (D5299); casing (D1785, F480); grout (C150 — Portland cement); water level measurement (D4750); well development in granular aquifers (D5521); well discharge (D5716 — circular orifice weir, D5737 — guide to methods); maintenance and rehabilitation (D5978)

Table B.1 Index to ASTM Field and Laboratory Methods Possibly Pertinent to Environmental Site Characterization (*Continued*)

Topic	ASTM Standard
Aquifer Hydraulic Properties	<u>Field Methods</u> : Packer tests (D4630, D4631); aquifer tests with control wells (D4105, D4106, D5269, D5270, D5472, D5473, D5920 — anisotropic unconfined, D6028, D6029 — leaky confining beds); slug tests (D4044, D4050, D4104, D5785, D5881, D5912); constant drawdown for flowing wells (D5787, D5855); constant rate pumping (D6034); partially penetrating wells (D5850); two-stage infiltration (D6391); test selection (D4043)
Modeling	Site-specific application (D5447); comparing simulation to site-specific information (D5490); documenting model application (D5718); defining boundary conditions (D5609); defining initial conditions (D5610); conducting sensitivity analysis (D5611); simulation of subsurface air flow (D5719); subsurface flow and transport modeling (D5880); model calibration (D5981); developing and evaluating codes (D6025); describing functionality (D6033); selecting a modeling code (D6170); documenting a modeling code (D6171)
Chemistry	<u>Field Methods</u> : Acidity/Alkalinity (D1067); electrical conductivity/resistivity (D1125); ion-selective electrodes (D4127); low-level dissolved oxygen (D5462); odor (D1292); pH (D1293, D5464); redox potential (D1498); test kits for inorganic constituents (D5463); turbidity (D1889); <u>Extraction Methods</u> : purgeable organics using headspace sampling (D3871); microextraction for volatiles and semivolatiles (D5241); <u>Laboratory Methods</u> : Organic carbon (D2579, D2579); minimum requirements for laboratories engaged in chemical analysis (D5522); see, generally, Volumes 11.01 and 11.02
Microbiology	ATP content (D4012); iron bacteria (D932); sulfate-reducing bacteria (D4412); microbial respiration (<i>D4478</i>); microscopy (D4454 — total respiring bacteria, D4455 — epifluorescence); plating methods (D5465); on-site screening heterotrophic bacteria (F488)
Surface Water	
Geometry/Flow Measurement	Depth measurement (D5073, D5906 — horizontal positioning, D6318 — fathometer calibration); measurement of morphologic characteristics of surface water bodies (D4581); operating a gauging station (D5674); <u>Discharge</u> : Step backwater method (D5388); <u>Open-Channel Flow</u> : Selection of weirs and flumes (D5640); acoustic methods (D4408); acoustic velocity method (D5389); broad-crested weirs (5614); culverts (D5243); developing a stage-discharge relation (D5541); dye tracers (D5613); electromagnetic current meters (D5089); Palmer–Bowles flume (D5390); Parshall flume (D1941); rotating element current meters (D4409); slope-area method (D5130); thin-plate weirs (D5242); velocity-area method (D3858); width contractions (D5129); <u>Open Water Bodies</u> : Water level measurement (D5413)
Other Characteristics	Suspended sediment concentration (<i>D3977</i>); environmental conditions relevant to spill control systems (F625); <u>Chemistry</u> : See ground water above
Waste/Contaminants	
Waste Properties	<u>Field/Screening Methods</u> : Compatibility (D5059); cyanides (<i>D5049</i>); flammability potential (D4982); oxidizers (D4981); pH (D4980); physical description screening analysis (D4979); radioactivity (D5928); sulfides (D4978); waste specific gravity/bulk density (D5057); <u>Laboratory Methods</u> : Waste bulk density (E1109); biological clogging of geotextiles (D1987); coal fly ash (D5759); solid waste freeze–thaw resistance (D4842); stability and miscibility (D5232); wetting and drying (D4843); <u>Extraction Methods</u> : Single-batch extraction methods (D5233); sequential batch extraction (D4793 — water, D5284 — acidic extraction fluid); soxhlet extraction (D5369); total solvent extractable content (D5368); solvent extraction of total petroleum hydrocarbons (D5765); shake extraction of solid waste and water (D3987)
Radioactive Materials	<u>Monitoring</u> : Detector calibration (E181); radiation measurement/dosimetry (D3648, E170); radiation protection programs for decommissioning operations (E1167); <u>Sampling/Preparation</u> : Sampling surface soil for radionuclides (C998); soil sample preparation for determination of radionuclides (C999)
Asbestos	Screen analysis (D2947)

Table B.1 Index to ASTM Field and Laboratory Methods Possibly Pertinent to Environmental Site Characterization (*Continued*)

Topic	ASTM Standard
Other Site Conditions	
Field Atmospheric Conditions	Atmospheric pressure (D3631); temperature (D6176M); conversion unit and factors (D1914); determining comparability of meteorological measurements (D4430); <i>Humidity</i> : Dew-point hygrometer (D4030); psychrometer (E337); terminology (D4023); <i>Wind</i> : Anemometers (<i>D4480</i> , D5096, D5741, D6011); surface wind by acoustic means (D5527); wind vane (D5741, D5366 — performance); see Volume 11.03 generally
Solar insolation	Pyranometers (E824, E913, E941); pyrhemimeters (E816)

Note: Italics indicate discontinued standard. Boldface = method selection guides.

ASTM Standards Indexed in Table B.1 (in Volume 4.08 or 4.09, unless otherwise specified)^a

C150-99a ^b	Specification for Portland Cement (Vol. 4.01)
C294-98	Descriptive Nomenclature for Constituents of Natural Mineral Aggregates (Vol. 4.02)
C998-90	Practice for Sampling Surface Soil for Radionuclides (Vol. 12.01)
C999-90	Practice for Soil Sample Preparation for Determination of Radionuclides (Vol. 12.01)
D140-98	Practice for Sampling Bituminous Materials
D420-98	Guide for Site Characterization for Engineering, Design, and Construction Purposes
D421-85	Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants
D422-63	Method for Particle-Size Analysis of Soils
D425-88	Test Method for Centrifuge Moisture Equivalent of Soils
D427-98	Test Method for Shrinkage Factors of Soils by the Mercury Method
D596-01	Guide for Reporting Results of Analysis of Water
D653-02	Terminology Relating to Soil, Rock, and Contained Fluids
D698-00a	Test Method for Laboratory Compaction Characteristics of Soil Using Standard Effort
D854-02	Test Method for Specific Gravity of Soil Solids by Water Pycnometer
D887-82	Practice for Sampling Water-Formed Deposits (Vol. 11.02)
D932-85	Test Method for Iron Bacteria in Water and Water-Formed Deposits (Vol. 11.02)
D933-84	Practice for Reporting Results of Examination and Analysis of Water-Formed Deposits (Vol. 11.04)
D1067-92	Test Methods for Acidity and Alkalinity in Water (Vol. 11.01)
D1125-95	Test Methods for Electrical Conductivity and Resistivity of Water (Vol. 11.01)
D1129-02a	Terminology Relating to Water (Vol. 11.01)
D1140-00	Test Method for Amount of Materials in Soils Finer than No. 200 (75- μ) Sieve
D1194-94	Test Method for Bearing Capacity for Soil for Static Load and Spread Footings
D1292-86	Test Method for Odor in Water (Vol. 11.01)
D1293-99	Test Methods for pH in Water (Vol. 11.01)
D1356-00a	Terminology Relating to Atmospheric Sampling (Vol. 11.03)
D1357-95	Practice for Planning the Sampling of the Ambient Atmosphere (Vol. 11.03)
D1452-80	Practice for Soil Investigation and Sampling by Auger Borings
D1498-00a	Practice for Oxidation-Reduction Potential of Water (Vol. 11.01)
D1556-00	Test Method for Density of Soil in Place by the Sand-Cone Method
D1557-02	Test Method for Laboratory Compaction Characteristics of Soil Using Modified Effort
D1558-99	Test Method for Moisture Content Penetration Resistance Relationships of Fine-Grained Soils
D1586-99	Test Method for Penetration Test and Split-Barrel Sampling of Soils
D1587-94	Practice for Thin-Walled Tube Geotechnical Sampling of Soils
D1704-94	<i>Test Method for Determining the Amount of Particulate Matter in the Atmosphere by Measurement of Light Absorption of a Filtered Sample (Vol. 11.03); discontinued 2000</i>
D1704M-94	<i>Test Method for Determining the Amount of Particulate Matter in the Atmosphere by Measurement of the Absorbance of a Filter Sample (Metric) (Vol. 11.03); discontinued 2000</i>
D1739-98	Test Method for Collection and Analysis of Dustfall (Settleable Particulates) (Vol. 11.03)
D1785-99	Specifications for Polyvinyl Chloride (PVC) Plastic Pipe Schedules 40, 80 and 120 (Vol. 8.04)
D1883-99	Test Method for CBR (California Bearing Ratio) of Laboratory-Compacted Soils
D1889-00	Test Methods for Turbidity in Water (Vol. 11.01)

ASTM Standards Indexed in Table B.1 (in Volume 4.08 or 4.09, unless otherwise specified)^a (Continued)

D1914-95	Practice for Conversion Units and Factors Relating to Atmospheric Analysis (Vol. 11.03)
D1941-91	Test Method for Open Channel Flow Measurements of Water with the Parshall Flume (Vol. 11.01)
D1987-95	Test Method for Biological Clogging of Geotextiles of Soil/Geotextile Filters
D2113-99	Practice for Diamond Core Drilling for Site Investigation
D2166-00	Test Method for Unconfined Compressive Strength of Cohesive Soil
D2167-94	Test Method for Density and Unit Weight of Soil in Place by the Rubber Balloon Method
D2216-98	Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock [Gravimetric oven drying]
D2217-85	Practice for Wet Preparation of Soil Samples for Particle-Size Analysis and Determination Soil Constants
D2325-68	Test Method for Capillary-Moisture Relationship for Coarse- and Medium-Textured Soils by Porous-Plate Apparatus [Soil water retention]
D2434-68	Test Method for Permeability of Granular Soils (Constant Head) [$>1 \times 10^{-3}$ cm/sec]
D2435-02	Test Method for One-Dimensional Consolidation Properties of Soils
D2487-00	Classification of Soils for Engineering Purposes (Unified Soil Classification System)
D2488-00	Practice for Description and Identification of Soils (Visual-Manual Procedures)
D2573-94	Test Method for Field Vane Shear Test in Cohesive Soil
D2579-93	Test Methods for Total and Organic Carbon in Water (Vol. 11.02)
D2607-69	<i>Classification of Peats, Mosses, Humus, and Related Products; discontinued 1992</i>
D2664-95a	Test Method for Triaxial Compressive Strength of Undrained Rock Core Specimen without Pore Pressure Measurements
D2845-00	Method for Laboratory Determination of Pulse Velocities and Ultrasonic Elastic Constants of Rock
D2850-95	Test Method for Unconsolidated, Undrained Compressive Strength of Cohesive Soils in Triaxial Compression
D2922-01	Test Methods for Density of Soil and Soil-Aggregate in Place by Nuclear Methods (Shallow Depth) [Gamma-gamma, surface or <12 in.]
D2936-95	Test Method for Direct Tensile Strength of Intact Rock Core Specimens
D2937-94	Test Method for Density of Soil in Place by the Drive-Cylinder Method
D2938-95	Test Method for Unconfined Compressive Strength of Intact Rock Core Specimens
D2947-88	Test Method for Screen Analysis of Asbestos Fibers (Vols. 4.05 and 8.02)
D2974-00	Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils
D2976-71	Test Method for pH of Peat Materials
D3017-01	Test Method for Water Content of Soil and Rock in Place by Nuclear Methods (Shallow Depth) [Neutron Probe]
D3080-98	Test Method for Direct Shear Test of Soils under Consolidated Drained Conditions
D3148-96	Test Methods for Elastic Moduli of Intact Rock Core Specimens in Uniaxial Compression
D3152-72	Test Method for Capillary-Moisture Relationships for Fine-Textured Soils by Pressure Membrane Apparatus
D3213-91	Practice for Handling, Storing, and Preparing Soft Undisturbed Marine Soil
D3249-95	Practice for General Ambient Air Analyzer Procedures (Vol. 11.03)
D3325-90	Practice for the Preservation of Waterborne Oil Samples (Vol. 11.02)
D3326-90	Practices for Preparation of Samples for Identification of Waterborne Oils (Vol. 11.02)
D3370-95a	Practices for Sampling Water from Closed Conduits (Vol. 11.01)
D3385-94	Test Method for Infiltration Rate of Soils in Field Using Double-Ring Infiltrometers
D3404-91	Guide to Measuring Matric Potential in the Vadose Zone Using Tensiometers
D3441-98	Test Method for In-Situ Cone Penetration Testing of Soil
D3550-84	Practice for Ring-Lined Barrel Sampling of Soils
D3584-83	<i>Practice for Indexing Papers and Report on Soil and Rock for Engineering Purposes; discontinued 1996</i>
D3614-97	Guide for Laboratories Engaged in Sampling and Analysis of Atmospheres and Emissions (Vol. 11.03)
D3631-99	Method for Measuring Surface Atmospheric Pressure (Vol. 11.03)
D3648-95	Practices for Measurement of Radioactivity (Vol. 11.02)
D3686-95	Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method) (Vol. 11.03)
D3694-96	Practice for Preparation of Sample Containers and for Preservation of Organic Constituents (Vol. 11.02)
D3740-01	Practice for Evaluation of Agencies Engaged in the Testing and/or Inspection of Soil and Rock Used in Engineering Design and Construction
D3856-95	Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water (Vol. 11.01)

ASTM Standards Indexed in Table B.1 (in Volume 4.08 or 4.09, unless otherwise specified)^a (Continued)

D3858-95	Practice for Open Channel Flow Measurements of Water by Velocity-Area Method (Vol. 11.01)
D3864-96	Guide for Continual On-Line Monitoring Systems for Water Analysis (Vol. 11.01)
D3871-84	Test Method for Purgeable Organic Compounds in Water Using Headspace Sampling (Vol. 11.02)
D3967-95a	Test Method for Splitting Tensile Strength of Intact Rock Core Specimens
D3975-93	Practice for Development and Use (Preparation) of Samples for Collaborative Testings of Methods for Analysis of Sediments (Vol. 11.02)
D3976-92	Practice for Preparation of Sediments Samples for Chemical Analysis (Vol. 11.02)
D3977-80	<i>Practice for Determining Suspended Sediment Concentration in Water Samples (Vol. 11.02); discontinued 1995</i>
D3987-85	Method for Shake Extraction of Solid Waste and Water (Vol. 11.04)
D4012-81	Test Method for Adenosine Triphosphate (ATP) Content of Microorganisms in Water (Vol. 11.02)
D4023-82a	Definitions of Terms Relating to Humidity Measurements (Vol. 11.03)
D4043-96	Guide for Selection of Aquifer-Test Field and Analytical Procedures in Determination of Hydraulic Properties by Well Techniques
D4044-96	Test Method (Field Procedures) for Instantaneous Change in Head (Slug Tests) for Determining Hydraulic Properties of Aquifers
D4050-96	Test Method (Field Procedure) for Withdrawal and Injection Well Tests for Determining Hydraulic Properties of Aquifer Systems
D4083-89	Practice for Description of Frozen Soils (Visual-Manual Procedure)
D4096-91	Test Method for Determination of Total Suspended Particulate Matter in the Atmosphere (High-Volume Sampler Method) (Vol. 11.03)
D4104-96	Test Method (Analytical Procedure) for Determining Transmissivity of Nonleaky Confined Aquifers by Overdamped Well Response to Instantaneous Change in Head (Slug Test)
D4105-96	Test Method (Analytical Procedure) for Determining Transmissivity and Storage Coefficient of Nonleaky Confined Aquifers by the Modified Theis Nonequilibrium Method
D4106-96	Test Method (Analytical Procedure) for Determining Transmissivity and Storage Coefficient of Nonleaky Confined Aquifers by the Theis Nonequilibrium Method
D4127-92	Terminology Used with Ion-Selective Electrodes (Vol. 11.01)
D4129-98	Test Method for Total and Organic Carbon in Water by High Temperature Oxidation and by Coulometric Detection (Vol. 11.02)
D4220-95	Practices for Preserving and Transporting Soil Samples
D4221-99	Test Method for Dispersive Characteristics of Clay Soil by Double Hydrometer
D4230-02	Test Method of Measuring Humidity with Cooled-Surface Condensation (Dew Point) Hygrometer (Vol. 11.03)
D4318-00	Test Method for Liquid Limit, Plastic Limit, and Plasticity Index of Soils
D4341-93	Test Method for Creep of Cylindrical Hard Rock Core Specimens in Uniaxial Compression
D4373-02	Test Method for Rapid Determination of Carbonate Content of Soils
D4375-96	Terminology for Basic Statistics in Committee D-19 on Water (Vol. 11.01)
D4394-84	Test Method for Determining the <i>In Situ</i> Modulus of Deformation of Rock Mass Using the Rigid Plate Loading Method
D4395-84	Test Method for Determining the <i>In Situ</i> Modulus of Deformation of Rock Mass Using the Flexible Plate Loading Method
D4403-84	Practice for Extensometers Used in Rock
D4404-84	Test Method for Determination of Pore Volumes and Pore Volume Distribution of Soil and Rock by Mercury Intrusion Porosimetry
D4405-93	Test Method for Creep of Cylindrical Soft Rock Core Specimens in Uniaxial Compression
D4406-93	Test Method for Creep of Cylindrical Soft Rock Core Specimens in Triaxial Compression
D4408-84	Practice for Open Channel Flow Measurements by Acoustic Means (Vol. 11.01)
D4409-95	Test Method for Velocity Measurement of Water in Open Channels with Rotating Element Current Meters (Vol. 11.01)
D4410-98	Terminology of Fluvial Sediment (Vol. 11.01)
D4411-98	Guide for Sampling Fluvial Sediment in Motion (Vol. 11.02)
D4412-84	Test Methods for Sulfate-Reducing Bacteria in Water and Water-Formed Deposits (Vol. 11.02)
D4428/	
D4428M-00	Test Method for Crosshole Seismic Testing
D4429-93	Test Method for Bearing Ratio of Soils in Place
D4430-96	Practice for Determining the Comparability of Meteorological Measurements (Vol. 11.03)
D4448-01	Guide for Sampling Groundwater Monitoring Wells (Vol. 11.04)
D4452-85	Methods for X-Ray Radiography of Soil Samples
D4454-85	Test Method for Simultaneous Enumeration of Total Respiring Bacteria in Aquatic Systems by Microscopy (Vol. 11.02)

ASTM Standards Indexed in Table B.1 (in Volume 4.08 or 4.09, unless otherwise specified)^a (Continued)

D4455-85	Test Method for Enumeration of Aquatic Bacteria by Epifluorescence Microscopy Counting Procedure (Vol. 11.02)
D4478-85	<i>Test Methods for Oxygen Uptake (Vol. 11.02) [Microbial respiration]; discontinued 1994</i>
D4480-85	<i>Test Method for Measuring Surface Wind by Means of Wind Vanes and Rotating Anemometers (Vol. 11.03); discontinued 1999; replaced by D5741</i>
D4489-95	Practices for Sampling Waterborne Oils (Vol. 11.02)
D4490-96	Practice for Measuring the Concentration of Toxic Gases or Vapors Using Detector Tubes (Vol. 11.03)
D4506-02	Test Method for Determining the <i>In Situ</i> Modulus of Deformation of Rock Mass Using a Radial Jacking Test
D4511-00	Test Method for Hydraulic Conductivity of Essentially Saturated Peat (Constant Head)
D4515-85	Practice for Estimation of Holding Time for Water Samples Containing Organic Constituents (Vol. 11.02)
D4525-90	Test Method for Permeability of Rocks by Flowing Air
D4531-86	Test Method for Bulk Density of Peat and Peat Products
D4536-96	Test Method for High Volume Sampling for Solid Particulate Matter and Determination of Particulate Emissions (Vol. 11.03)
D4542-95	Test Method for Pore Water Extraction and Determination of the Soluble Salt Content of Soils by Refractometer
D4543-01	Practice for Determining Dimensional and Shape Tolerances of Rock Core Specimens
D4544-86	Practice for Estimating Peat Deposit Thickness
D4546-96	Test Methods for One-Dimensional Swell or Settlement Potential of Cohesive Soils
D4547-98	Practice for Sampling Waste and Soils for Volatile Organics (Vol. 11.04)
D4553-02	Test Method for Determining the <i>In Situ</i> Creep Characteristics of Rock
D4554-02	Test Method for <i>In Situ</i> Determination of Direct Shear Strength of Rock Discontinuities
D4555-01	Test Method for Determining Deformability and Strength of Weak Rock by an <i>In Situ</i> Uniaxial Compressive Test
D4564-02	Test Method for Density of Soil in Place by the Sleeve Method [Cohesionless, gravelly soils]
D4581-86	Guide for Measurement of Morphologic Characteristics of Surface Water Bodies (Vol. 11.02)
D4597-97	Practice for Sampling Workplace Atmospheres to Collect Gases of Vapors with Activated Charcoal Samplers (Vol. 11.03)
D4598-87	<i>Practice for Sampling Workplace Atmospheres to Collect Gases of Vapors with Liquid Sorbent Diffusional Samplers (Vol. 11.03); Discontinued 1995</i>
D4599-97	Practice for Measuring the Concentration of Toxic Gases or Vapors Using Length-of-Stain Dosimeter (Vol. 11.03)
D4623-02	Test Method for Determination of <i>In Situ</i> Stress in Rock Mass by Overcoring Method (USBM Borehole Deformation Gage)
D4630-96	Test Method for Determining Transmissivity and Storativity of Low Permeability Rocks by <i>In-Situ</i> Measurements Using the Constant Head Injection Test
D4631-95	Test Method for Determining Transmissivity and Storativity of Low Permeability Rocks by <i>In-Situ</i> Measurements Using the Pressure Pulse Technique
D4633-86	<i>Test Method for Stress Wave Energy Measurement for Dynamic Penetrometer Testing Systems; discontinued 1998</i>
D4638-95a	Guide for Preparation of Biological Samples for Inorganic Chemical Analysis (Vol. 11.01)
D4643-00	Test Method for Determination of Water (Moisture) Content of Soil by the Microwave Oven Method
D4645-87	Test Method for Determination of the <i>In Situ</i> Stress in Rock Using the Hydraulic Fracturing Method
D4647-93	Test Method for Identification and Classification of Dispersive Clay Soils by the Pinhole Test
D4648-00	Test Method for Laboratory Miniature Vane Shear Test for Saturated Fine-Grained Clayey Soil
D4687-95	Guide for General Planning of Waste Sampling (Vol. 11.04)
D4696-92	Guide for Pore-Liquid Sampling from the Vadose Zone
D4700-91	Guide for Soil Sampling from the Vadose Zone
D4719-87	Test Method for Pressuremeter Testing in Soils
D4729-87	Test Method for <i>In Situ</i> Stress and Modulus of Deformation Using the Flatjack Method
D4750-87	Test Method for Determining Subsurface Liquid Levels in a Borehole or Monitoring Well (Observation Well)
D4767-95	Test Method for Consolidated-Undrained Triaxial Compression Test on Cohesive Soils
D4793-93	Method for Sequential Batch Extraction of Waste with Water (Vol. 11.04)
D4822-88	Guide for Selection of Methods of Particle Size Analysis of Fluvial Sediments (Manual Methods) (Vol. 11.02)
D4823-95	Guide for Core-Sampling Submerged, Unconsolidated Sediments (Vol. 11.02)
D4840-99	Guide for Sample Chain of Custody Procedure (Vol. 11.01)

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D4841-88	Practice to Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents (Vol. 11.01)
D4842-90	Test Method for Determining the Resistance of Solid Wastes to Freezing and Thawing (Vol. 11.04)
D4843-88	Test Method for Wetting and Drying Test of Solid Waste (Vol. 11.04)
D4844-88	Guide for Air Monitoring at Waste Management Facilities for Worker Protection (Vol. 11.04)
D4861-00	Practice for Sampling and Selection of Analytical Techniques for Pesticides and Polychlorinated Biphenyls in Air (Vol. 11.03)
D4879-02	Guide for Geotechnical Mapping of Large Underground Openings in Rock
D4914-99	Test Methods for Density of Soil and Rock in Place by the Sand Replacement Method in a Test Pit [Soils with particles larger than 3 in.]
D4943-02	Test Method for Shrinkage Factors of Soils by the Wax Method
D4944-98	Test Method for Field Determination of Water (Moisture) Content of Soil by the Calcium Carbide Gas Pressure Tester Method
D4959-00	Test Method for Determination of Water (Moisture) Content of Soil by Direct Heating Method
D4971-02	Test Method for Determining the <i>In Situ</i> Modulus of Deformation of Rock Using the Diametrically Loaded 76-mm (3-in) Borehole Jack
D4972-01	Test Method for pH of Soils
D4978-95	Test Method for Screening of Reactive Sulfide in Waste (Vol. 11.04)
D4979-95	Test Method for Physical Description Screening Analysis in Waste (Vol. 11.04)
D4980-89	Test Method for Screening of pH in Waste (Vol. 11.04)
D4981-95	Test Method for Screening of Oxidizers in Waste (Vol. 11.04)
D4982-95	Test Methods for Flammability Potential Screening Analysis of Waste (Vol. 11.04)
D5012-01	Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition (Vol. 11.03)
D5013-89	Practice for Sampling Wastes from Pipes and Other Point Discharges (Vol. 11.04)
D5030-89	Test Method for Density of Soil and Rock in Place by the Water Replacement Method in a Test Pit
D5049-90	<i>Test Method for Screening of Cyanides in Waste (Vol. 11.04); discontinued 1999</i>
D5057-90	Method for Screening of Apparent Specific Gravity and Bulk Density of Waste (Vol. 11.04)
D5059-98	Test Methods for Compatibility Screening Analysis of Waste (Vol. 11.04)
D5073-02	Practice for Depth Measurement of Surface Water (Vol. 11.02)
D5079-02	Practices for Preserving and Transporting Rock Core Samples
D5080-00	Test Method for Rapid Determination of Percent Compaction
D5084-00	Test Method for Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter [Low permeability materials, $<1 \times 10^{-3}$ cm/sec]
D5088-02	Practice for Decontamination of Field Equipment Used at Nonradioactive Waste Sites
D5089-95	Test Method for Velocity Measurements of Water in Open Channels with Electromagnetic Current Meters (Vol. 11.01)
D5092-90	Recommended Practice for Design and Installation of Ground Water Monitoring Wells in Aquifers
D5093-02	Test Method for Field Measurement of Infiltration Rate Using a Double-Ring Infiltrometer with a Sealed-Inner Ring
D5096-02	Test Method for Determining the Performance of a Cup Anemometer or Propeller Anemometer (Vol. 11.03)
D5111-99	Guide for Choosing Locations and Sampling Methods to Monitor Atmospheric Deposition at Non-Urban Locations (Vol. 11.03)
D5126-90	Guide for Comparison of Field Methods for Determining Hydraulic Conductivity in the Vadose Zone [Saturated: single- or double-ring infiltrometer, double-tube, air-entry permeameter, borehole permeameter (constant-head borehole infiltration, Guelph permeameter), empirical; unsaturated: instantaneous profile, crust, empirical]
D5129-95	Test Method for Open Channel Flow Measurement of Water Indirectly by Using Width Contractions (Vol. 11.01)
D5130-95	Test Method for Open Channel Flow Measurement of Water Indirectly by Slope-Area Method (Vol. 11.01)
D5143-91	Test Method for Analysis of Nitroaromatic and Nitramine Explosive in Soil by High Performance Liquid Chromatography
D5195-02	Test Method for Determination of Density of Soil and Rock In-Place at Depths below the Surface by Nuclear Methods [Gamma-gamma, >12 in.]
D5220-02	Test Method for Water Content of Soil and Rock in Place by the Neutron Depth Probe Method
D5232-92	Test Method for Determining the Stability and Miscibility of a Solid, Semi-Solid, or Liquid Waste Materials (Vol. 11.04)
D5233-92	Test Method for Single Batch Extraction Methods for Wastes (Vol. 11.04)
D5239-98	Practice for Characterizing Fly Ash for Use in Soil Stabilization

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D5241-92	Practice for Micro-Extraction of Water for the Analysis of Volatile and Semi-Volatile Organic Compounds in Water (Vol. 11.02)
D5242-92	Test Method for Open Channel Flow Measurement of Water Indirectly at Culverts (Vol. 11.01)
D5243-92	Test Method for Open Channel Flow Measurements of Water Indirectly at Culverts (Vol. 11.01)
D5254-92	Practice for the Minimum Set of Data Elements to Identify a Ground Water Site
D5255-01	Practice for Certification of Personnel Engaged in the Testing of Soil and Rock
D5269-96	Test Method for Determining Transmissivity of Non-Leaky Confined Aquifers by the Theis Recovery Method
D5270-96	Test Method for Determining Transmissivity and Storage Coefficient of Bounded, Non-Leaky Confined Aquifers
D5283-92	Practice for Generation of Environmental Data Related to Waste Management Activities: QA/QC Planning and Implementation (Vol. 11.04)
D5284-93	Test Method for Sequential Batch Extraction of Waste with Acidic Extraction Fluid (Vol. 11.04)
D5298-94	Test Method for Measurement of Soil Potential (Suction) Using Filter Paper
D5299-99	Guide for the Decommissioning of Ground Water Wells, Vadose Zone Monitoring Devices, Boreholes and Other Devices for Environmental Activities
D5311-92	Test Method for Load Controlled Cyclic Triaxial Strength of Soil
D5314-92	Guide for Soil Gas Monitoring in the Vadose Zone
D5334-00	Test Method for Determination of Thermal Conductivity of Soil and Rock by Thermal Needle Probe Procedure
D5335-99	Test Method for Linear Coefficient of Thermal Expansion of Rock Using Bonded Electric Resistance Strain Gages
D5337-97	Practice for Flow Rate for Calibration of Personal Sampling Pumps (Vol. 11.03)
D5358-93	Practice for Sampling with a Dipper or Pond Sampler (Vol. 11.04)
D5366-96	Test Method for Determining the Dynamic Performance of a Wind Vane (Vol. 11.03)
D5368-93	Test Method for the Gravimetric Determination of Total Solvent Extractable Content (TSEC) of Solid Waste Samples (Vol. 11.04)
D5369-93	Test Method for the Extraction of Solid Waste Samples for Chemical Analysis Using Soxhlet Extraction (Vol. 11.04)
D5387-93	Guide for Elements of a Complete Data Set for Non-Cohesive Sediments (Vol. 11.02)
D5388-93	Method for Measurement of Discharge by Step-Backwater Method (Vol. 11.01)
D5389-93	Method for Open Channel Flow Measurement by Acoustic Velocity Meter Systems (Vol. 11.02)
D5390-93	Method for Open Channel Flow Measurement of Water with Palmer-Bowles Flumes (Vol. 11.02)
D5407-95	Test Method for Elastic Moduli of Undrained Intact Rock Core Specimens in Triaxial Compression without Pore Pressure Measurement
D5408-93	Guide for the Set of Data Elements to Describe a Ground-Water Site, Part 1 — Additional Identification Descriptors
D5409-93	Guide for the Set of Data Elements to Describe a Ground-Water Site, Part 2 — Physical Descriptors
D5410-93	Guide for the Set of Data Elements to Describe a Ground-Water Site, Part 3 — Usage Descriptors
D5413-93	Test Methods for Measurement of Water Levels in Open-Water Bodies (Vol. 11.01)
D5434-97	Guide for Field Logging of Subsurface Explorations of Soil and Rock
D5435-93	Test Method for Diagnostic Soil Test for Plant Growth and Food Chain Protection
D5447-93	Guide for Application of a Ground-Water Flow Model to a Site Specific Problem
D5451-93	Practice for Sampling Using a Trier Sampler (Vol. 11.04)
D5462-02	Test Method for On-Line Measurement of Low Level Dissolved Oxygen in Water (Vol. 11.01)
D5463-93	Guide for the Use of Test Kits to Measure Inorganic Constituents in Water (Vol. 11.02)
D5464-93	Test Methods for pH Measurement of Water of Low Conductivity (Vol. 11.01)
D5465-93	Practices for Determining Microbial Counts for Waters Analyzed by Plating Methods (Vol. 11.02)
D5466-01	Test Method for Determination of Volatile Organic Chemicals in Atmospheres (Canister Sampling Methodology) (Vol. 11.03)
D5472-93	Test Method for Determining Specific Capacity and Estimating Transmissivity at the Control Well
D5473-93	Test Method (Analytical Procedure) for Analyzing the Effects of Partial Penetration of Control Well and Determining the Horizontal and Vertical Hydraulic Conductivity in a Nonleaky Aquifer
D5474-93	Guide for Selection of Data Elements for Ground-Water Investigations
D5490-93	Guide for Comparing Ground-Water Flow Model Simulations to Site-Specific Information
D5495-94	Practice for Sampling with a Composite Liquid Waste Sampler (COLIWASA) (Vol. 11.04)
D5518-94	Guide for Acquisition of File Aerial Photography and Imagery for Establishing Historic Site-Use and Surficial Conditions
D5520-94	Test Method for Laboratory Determination of Creep Properties of Frozen Soil Samples by Uniaxial Compression

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D5521-94	Guide for Development of Ground-Water Monitoring Wells in Granular Aquifers
D5522-99a	Specification for Minimum Requirements for Laboratories Engaged in Chemical Analysis of Soil, Rock and Contained Fluid
D5527-94	Practice for Measuring Surface Wind and/or Temperature by Acoustic Means (Vol. 11.03)
D5540-94a	Practice for Flow Control and Temperature Control for On-Line Water Sampling and Analysis (Vol. 11.01)
D5541-94	Practice for Developing a Stage-Discharge Relation for Open Channel Flow (Vol. 11.01)
D5549-94	Guide for Reporting Geostatistical Site Investigations
D5550-00	Test Method for Specific Gravity of Soils Solids by Gas Pycnometer
D5607-02	Test Method for Performing Laboratory Direct Shear Strength Tests of Rock Specimens under Constant Normal Force
D5608-01	Standard Practice for the Decontamination of Field Equipment Used at Low Level Radioactive Waste Sites
D5609-94	Guide for Defining Boundary Conditions in Ground-Water Flow Modeling
D5610-94	Guide for Defining Initial Conditions in Ground-Water Flow Modeling
D5611-94	Guide for Conducting a Sensitivity Analysis for a Ground-Water Flow Model Application
D5612-94	Guide for the Quality Planning and Field Implementation of a Water Quality Measurement Program (Vol. 11.01)
D5613-94	Test Method for Open Channel Measurements of Time of Travel Using Dye Tracers (Vol. 11.02)
D5614-94	Test Method for Open Channel Flow Measurement of Water with Broad-Crested Weirs (Vol. 11.02)
D5633-94	Practice for Sampling with a Scoop (Vol. 11.04)
D5640-95	Guide for Selection of Weirs and Flumes for Open Channel Flow Measurement of Water (Vol. 11.02)
D5658-95	Practice for Sampling Unconsolidated Waste from Trucks (Vol. 11.04)
D5674-95	Guide for Operations of a Gaging Station (Vol. 11.02)
D5679-95a	Practice for Sampling Consolidated Solids in Drums or Similar Containers (Vol. 11.04)
D5680-95a	Practice for Sampling Unconsolidated Solids in Drums or Similar Containers (Vol. 11.04)
D5681-98a	Terminology for Waste and Waste Management (Vol. 11.04)
D5714-95	Specification for Digital Geospatial Metadata
D5715-00	Test Method for Estimating the Degree of Humification of Peat and Other Organic Soils (Visual/Manual Method)
D5716-95	Test Method to Measure the Rate of Well Discharge by Circular Orifice Weir
D5717-95	Guide for the Design of Ground-Water Monitoring Systems in Karst and Fractured-Rock Aquifers
D5718-95	Guide for Documenting a Ground-Water Flow Model Application
D5719-95	Guide to Simulation of Subsurface Air Flow Using Ground-Water Flow Modeling Codes
D5720-95	Practice for Static Calibration of Electronic Transducer-Based Pressure Measurements Systems for Geotechnical Purposes
D5731-02	Test Method for Determination of the Point Load Strength Index of Rock
D5737-95	Guide to Methods for Measuring Well Discharge
D5738-95	Guide for Displaying the Results of Chemical Analyses of Ground Water for Major Ions and Trace Elements — Diagrams for Single Analyses
D5741-96	Practice for Characterizing Surface Wind Using a Wind Vane and Rotating Anemometer (Vol. 11.03)
D5743-97	Practice for Sampling Single or Multilayered Liquids, with or without Solids in Drums or Similar Containers (Vol. 11.04)
D5745-95	Guide for Developing and Implementing Short-Term Measures or Early Actions for Site Remediation (Vol. 11.04)
D5746-98	Classification of Environmental Condition of Property Area Types for Defense Base Closure and Realignment Facilities (Vol. 11.04)
D5753-95	Guide for Planning and Conducting Borehole Geophysical Logging
D5754-95	Guide for Displaying the Results of Chemical Analyses of Ground Water for Major Ions and Trace Elements — Trilinear and Other Multi-Coordinate Diagrams
D5759-95	Guide for Characterization of Coal Fly Ash and Clean Coal Combustion Fly Ash for Potential Use (Vol. 11.04)
D5765-95	Practice for Solvent Extraction of Total Petroleum Hydrocarbons from Soils and Sediments Using Closed Vessel Microwave Heating (Vol. 11.01)
D5777-95	Guide for Using the Seismic Refraction Method for Subsurface Investigations
D5778-95	Test Method for Performing Electric Friction Cone and Piezocone Penetration Testing of Soils
D5781-95	Guide for Use of Dual-Wall Reverse-Circulation Drilling for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices

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D5782-95	Guide for Use of Direct Air-Rotary Drilling for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices
D5783-95	Guide for Use of Direct Rotary Drilling with Water-Based Drilling Fluid for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices
D5784-95	Guide for Use of Hollow-Stem Augers for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices
D5785-95	Test Method (Analytical Procedure) for Determining Transmissivity of Confined Nonleaky Aquifers by Under-Damped Well Response to Instantaneous Change in Head (Slug Test)
D5786-95	Practice (Field Procedure) for Constant Drawdown Tests in Flowing Wells for Determining Hydraulic Properties of Aquifer Systems
D5787-95	Practice for Monitoring Well Protection
D5789-95	Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents (Vol. 11.01)
D5791-95	Guide for Using Probability Sampling Methods in Studies of Indoor Air Quality of Buildings (Vol. 11.03)
D5792-02	Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives (Vol. 11.04)
D5829-96	Guide for Preparing a Training Program for Environmental Analytical Laboratories (Vol. 11.04)
D5831-96	Test Method for Screening Fuels in Soils (Vol. 11.04)
D5835-95	Practice for Sampling Stationary Source Emissions for the Automated Determination of Gas Concentrations (Vol. 11.03)
D5850-95	Test Method (Analytical Procedure) for Determining Transmissivity, Storage Coefficient, and Anisotropy Ratio from a Network of Partially Penetrating Wells
D5851-95	Guide for Planning and Implementing a Water Monitoring Program (Vol. 11.02)
D5852-95	Test Method for Erodibility Determination of Soil in the Field or in the Laboratory by the Jet Index Method
D5855-95	Test Method (Analytical Procedure) for Determining Transmissivity and Storage Coefficient of a Confined Nonleaky or Leaky Aquifer by the Constant Drawdown Method in a Flowing Well
D5856-95	Test Method for Measurement of Hydraulic Conductivity of Porous Material Using a Rigid-Wall, Compaction-Mold Permeameter
D5872-95	Guide for Use of Casing Advancement Drilling Methods for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices
D5873-00	Test Method for Determination of Rock Hardness by the Rebound Hammer Method
D5874-02	Test Method for Determination of the Impact Value (IV) of a Soil
D5875-95	Guide for Use of Cable-Tool Drilling and Sampling Methods for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices
D5876-95	Guide for Use of Direct Rotary Wireline Casing Advancement Drilling Methods for Geoenvironmental Exploration and Installation of Subsurface Water-Quality Monitoring Devices
D5877-95	Guide for Displaying the Results of Chemical Analyses of GroundWater for Major Ions and Trace Elements — Diagrams Based on Data Analytical Calculations
D5878-00	Guide for Using Rock-Mass Classification Systems for Engineering Purposes
D5879-95	Practice for Surface Site Characterization for On-Site Septic Systems
D5880-95	Guide for Subsurface Flow and Transport Modeling
D5881-95	Test Method (Analytical Procedure) for Determining Transmissivity of Confined Nonleaky Aquifers by Critically Damped Well Response to Instantaneous Change in Head (Slug Test)
D5903-96	Guide for Planning and Preparing for a Ground-Water Sampling Event
D5905-98	Specification for Substitute Wastewater (Vol. 11.01)
D5906-02	Guide for Measuring Horizontal Positioning during Measurements of Surface Water Depths (Vol. 11.01)
D5907-96a	Test Method for Filterable and Non-Filterable Matter in Water (Vol. 11.01)
D5911-96	Practice for a Minimum Set of Data Elements to Describe a Soil Sampling Site
D5912-96	Test Method (Analytical Procedure) for Determining Hydraulic Conductivity of an Unconfined Aquifer by Overdamped Well Response to Instantaneous Change in Head (Slug Test)
D5918-96	Test Methods for Frost Heave and Thaw Weakening Susceptibility of Soils
D5920-96	Test Method (Analytical Procedure) for Tests of Anisotropic Unconfined Aquifers by the Neuman Method
D5921-96	Practice for Subsurface Site Characterization of Test Pits for On-Site Septic Systems
D5922-96	Guide for Analysis of Spatial Variation in Geostatistical Site Investigations
D5923-96	Guide for the Selection of Kriging Methods in Geostatistical Site Investigations
D5924-96	Guide for the Selection of Simulation Approaches in Geostatistical Site Investigations

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D5925-96	Practice for Preliminary Sizing and Delineation of Soil Absorption Field Areas for On-Site Septic Systems
D5928-96	Test Method for the Screening of Waste for Radioactivity (Vol. 11.04)
D5956-96	Guide for Sampling Strategies for Heterogeneous Wastes (Vol. 11.04)
D5978-96	Guide for Maintenance and Rehabilitation of Ground Water Monitoring Wells
D5979-96	Guide for Conceptualization and Characterization of Ground Water Flow Systems
D5980-96	Guide for Selection and Documentation of Existing Wells for Use in Environmental Site Characterization and Monitoring
D5981-96	Guide for Calibrating a Ground-Water Flow Model Application
D5995-98	Guide for Environmental Site Characterization in Cold Regions
D6000-96	Guide for the Presentation of Water-Level Information from Ground Water Sites
D6001-96	Guide for Direct Push Water Sampling for Geoenvironmental Investigations
D6008-96	Practice for Conducting Environmental Baseline Surveys (Vol. 11.04)
D6009-96	Guide for Sampling Waste Piles (Vol. 11.04)
D6011-96	Test Method for Determining the Performance of a Sonic Anemometer/Thermometer (Vol. 11.03)
D6025-96	Guide for Developing and Evaluating Ground-Water Modeling Codes
D6026-01	Practice for Using Significant Digits in Calculating and Reporting Geotechnical Test Data
D6027-96	Practice for Calibrating Linear Displacement Transducers for Geotechnical Purposes
D6028-96	Test Method (Analytical Procedure) for Determining Hydraulic Properties of a Confined Aquifer Taking into Consideration Storage of Water in Leaky Confining Beds by the Modified Hantush Method
D6029-96	Test Method (Analytical Procedure) for Determining Hydraulic Properties of a Confined Aquifer and a Leaky Confining Bed with Negligible Storage by the Hantush-Jacob Method
D6030-96	Guide to Selection of Methods for Assessing Ground Water or Aquifer Sensitivity and Vulnerability
D6031-96	Test Method for Logging <i>In Situ</i> Moisture Content and Density of Soil and Rock by the Nuclear Method in Horizontal, Slanted and Vertical Access Tubes
D6032-96	Test Method for Determining Rock Quality Designation (RDQ) of Rock Core
D6033-96	Guide for Describing the Functionality of a Ground-Water Modeling Code
D6034-96	Test Method (Analytical Procedure) for Determining the Efficiency of a Production Well in a Confined Aquifer from a Constant Rate Pumping Test
D6035-02	Test Method for Determining the Effect of Freeze-Thaw on the Hydraulic Conductivity of Compacted or Undisturbed Soil Specimens Using a Flexible Wall Permeameter
D6036-96	Guide for Displaying the Results of Chemical Analyses of Ground Water for Major Ions and Trace Elements — Use of Maps
D6044-96	Guide for Representative Sampling and Management of Waste and Contaminated Media (Vol. 11.04)
D6051-96	Guide for Composite Sampling and Field Subsampling for Environmental Waste Management Activities (Vol. 11.04)
D6061-96	Practice for Evaluating the Performance of Respirable Aerosol Samplers (Vol. 11.03)
D6062M-96	Guide for Personal Samplers of Health-Related Aerosol Fractions (Metric) (Vol. 11.01)
D6063-96	Guide for Sampling of Drums and Similar Containers by Field Personnel (Vol. 11.04)
D6066-96	Practice for Determining the Normalized Penetration Resistance of Sand for Liquefaction Potential Evaluation
D6067-96	Guide for Using the Electronic Cone Penetrometer for Environmental Site Characterization
D6089-97	Guide for Documenting a Ground-Water Sampling Event
D6106-97	Guide for Establishing the Nomenclature of Ground-Water Aquifers
D6145-97	Guide for Monitoring Sediment in Watersheds (Vol. 11.02)
D6146-97	Guide for Monitoring Aqueous Nutrients in Watersheds (Vol. 11.02)
D6151-97	Practice for Using Hollow-Stem Augers for Geotechnical Exploration and Soil Sampling
D6167-97	Guide for Conducting Borehole Geophysical Logging — Mechanical Caliper
D6168-97	Guide for Selection of the Minimum Set of Data Elements Required to Identify Locations Chosen for the Field Collection of Information to Describe Soil, Rock, and Their Contained Fluids
D6169-98	Guide for Selection of Soil and Rock Sampling Devices Used with Drill Rigs for Environmental Investigations
D6170-97	Guide for Selecting a Ground-Water Modeling Code
D6171-97	Guide for Documenting a Ground-Water Modeling Code
D6176M-97	Practice for Measuring Surface Atmospheric Temperature with Electrical Temperature Sensors (Metric) (Vol. 11.03)
D6187-97	Practice for Cone Penetrometer Technology Characterization of Petroleum Contaminated Site with Nitrogen Laser-Induced Fluorescence

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D6196-97	Practice for Selection of Sorbents and Pumped Sampling/Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air (Vol. 11.03)
D6209-98	Test Method for Determination of Gaseous and Particulate Polycyclic Aromatic Hydrocarbons in Ambient Air (Collection on Sorbent-Backed Filters with Gas Chromatographic/Mass Spectrometric Analysis) (Vol. 11.03)
D6232-00	Guide for Selection of Sampling Equipment for Waste and Contaminated Media Data Collection Activities (Vol. 11.04)
D6233-98	Guide for Data Assessment for Environmental Waste Management Activities (Vol. 11.04)
D6235-98a	Practice for Expedited Site Characterization of Vadose Zone and Ground Water Contamination at Hazardous Waste Contaminated Sites
D6236-98	Guide for Coring and Logging Cement- or Lime-Stabilized Soil
D6246-98	Practice for Evaluating the Performance of Diffusive Samplers (Vol. 11.03)
D6250-98	Practice for Derivation of Decision Point and Confidence Limit for Statistical Testing of Mean Concentration in Waste Management Decisions (Vol. 11.04)
D6274-98	Guide for Conducting Borehole Geophysical Logging — Gamma
D6282-98	Guide for Direct Push Soil Sampling for Environmental Site Characterizations
D6285-99	Guide for Locating Abandoned Wells
D6286-98	Guide for Selection of Drilling Methods for Environmental Site Characterization
D6311-98	Guide for Generation of Environmental Data Related to Waste Management Activities: Selection and Optimization of Sampling Design (Vol. 11.04)
D6312-98	Guide for Developing Appropriate Statistical Approaches for Ground-Water Detection Monitoring Programs
D6318-98	Practice for Calibrating a Fathometer Using a Bar Check Method (Vol. 11.01)
D6323-98	Guide for Laboratory Subsampling of Media Related to Waste Management Activities (Vol. 11.04)
D6326-98	Practice for the Selection of Maximum Transit-Rate Ratios and Depths for the U.S. Series of Isokinetic Suspended-Sediment Samplers (Vol. 11.01)
D6331-98	Test Method for Determination of Mass Concentration of Particulate Matter from Stationary Sources at Low Concentrations (Manual Gravimetric Method) (Vol. 11.03)
D6345-98	Guide for Selection of Method for Active, Integrative Sampling of Volatile Organic Compounds in Air (Vol. 11.03)
D6348-98	Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared (FTIR) Spectroscopy (Vol. 11.03)
D6391-99	Test Method for Field Measurement of Hydraulic Conductivity Limits of Porous Materials Using Two Stages of Infiltration from a Borehole
D6418-01	Practice for Using the Disposable En Core Sampler for Sampling and Storing Soil for Volatile Organic Analysis (Vol. 11.04)
D6429-99	Guide for Selecting Surface Geophysical Methods
D6430-99	Guide for Using the Gravity Method for Subsurface Investigation
D6431-99	Guide for Using the Direct Current Resistivity Method for Subsurface Investigation
D6432-99	Guide for Using the Surface Ground Penetrating Radar Method for Subsurface Investigation
D6452-99	Guide for Purging Methods for Wells Used for Ground-Water Quality Investigations
D6453-99	Guide for Format of Computerized Exchange of Soil and Rock Test Data
D6467-99	Test Method for Torsional Ring Shear Test to Determine Drained Residual Shear Strength of Cohesive Soils
D6517-00	Guide for Field Preservation of Ground-Water Samples
D6519-00	Practice for Sampling of Soils Using Hydraulically Operated Stationary Piston Sampler
D6527-00	Test Method for Determining Unsaturated and Saturated Hydraulic Conductivity in Porous Media by State-State Centrifugation
D6528-00	Test Method for Consolidated Undrained Direct Simple Shear Testing of Cohesive Soils
D6538-00	Guide for Sampling Wastewater with Automatic Samplers (Vol. 11.04)
D6539-00	Test Method for Measurement of Pneumatic Permeability of Partially Saturated Porous Materials by Flowing Air
D6552-00	Practice for Controlling and Characterizing Errors in Weighing Collected Aerosols (Vol. 11.03)
D6564-00	Guide for Field Filtration of Ground-Water Samples
D6565-00	Test Method for Determination of Water (Moisture) Content of Soil by the Time-Domain Reflectometry (TDR) Method
D6568-00	Guide for Planning, Carrying Out, and Reporting Traceable Chemical Analyses of Water Samples (Vol. 11.01)
D6569-00	Test Method for On-Line Measurement of pH (Vol. 11.01)
D6572-00	Test Method for Determining Dispersive Characteristics of Clayey Soils by the Crumb Test

ASTM Standards Indexed in Table B.1 (in Volume 4.08 or 4.09, unless otherwise specified)^a (Continued)

D6582-00	Guide for Ranked Set Sampling: Efficient Estimation of a Mean Concentration in Environmental Sampling (Vol. 11.04)
D6597-00	Practice for Assessment of Attaining Clean Up Level for Site Closure (Vol. 11.04)
D6634-01	Guide for the Selection of Purging and Sampling Devices for Ground-Water Monitoring Wells
D6639-01	Guide for Using the Frequency Domain Electromagnetic Method for Subsurface Investigations
D6640-01	Practice for Collection and Handling of Soils Obtained in Core Barrel Samplers for Environmental Investigations
D6642-01	Guide for Comparison of Techniques to Quantify the Soil-Water Moisture Flux
D6661-01	Practice for Field Collection of Organic Compounds from Surfaces Using Wipe Sampling
D6698-01	Test Method for On-Line Measurement of Turbidity below 5 NTU in Water
D6699-01	Practice for Sampling Liquids Using Bailers
D6724-01	Guide for Installation of Direct Push Ground Water Monitoring Wells
D6725-01	Practice for Direct Push Installation of Prepacked Screen Monitoring Wells in Unconsolidated Aquifers
D6726-01	Guide for Conducting Borehole Geophysical Logging — Electromagnetic Induction
D6727-01	Guide for Conducting Borehole Geophysical Logging — Neutron
D6758-02	Test Method for Measuring Stiffness and Apparent Modulus of Soil and Soil-Aggregate In-Place by an Electro-Mechanical Method
D6759-02	Practice for Sampling Liquids Using Grab and Discrete Depth Samplers
D6764-02	Guide for Collection of Water Temperature, Dissolved-Oxygen Concentrations, Specific Electrical Conductance, and pH Data from Open Channels
D6771-02	Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations
D6780-02	Test Method for Water Content and Density of Soil by Time Domain Reflectometry (TDR)
D6820-02	Guide for Use of the Time Domain Electromagnetic Method for Subsurface Investigation
D6836-02	Test Methods for Determination of the Soil Water Characteristic Curve for Desorption Using a Hanging Column, Pressure Extractor, Chilled Mirror Hygrometer, and/or Centrifuge
E105-58	Practice for Probability Sampling of Materials (Vols. 7.02 and 14.02)
E170-99	Terminology Relating to Radiation Measurements and Dosimetry (Vol. 12.02)
E177-90a	Practice for Use of the Terms Precision and Bias in ASTM Test Methods (Vol. 14.02)
E178-94	Practice for Dealing with Outlying Observations (Vol. 14.02)
E181-98	General Methods for Detector Calibration and Analysis of Radionuclides (Vol. 12.02)
E337-02	Test Method of Measuring Humidity with a Psychrometer (the Measurement of Wet- and Dry-Bulb Temperatures) (Vol. 11.03)
E380-92	<i>Practice for Use of International System of Unit (SI) (Modernized Metric System); replaced by IEEE/ASTM SI-10</i>
E678-98	Practice for Evaluation of Technical Data (Vol. 14.02) [Focuses on product liability matters]
E816-95	Method for Calibration of Secondary Reference Pyrheliometers and Pyrheliometers for Field Use (Vol. 14.04)
E824-94	Method for Transfer of Calibration from Reference to Field Pyranometers (Vol. 14.04)
E884-82	Practice for Sampling Airborne Microorganisms at Municipal Solid Waste Processing Facilities (Vol. 11.04)
E913-82	Method for Calibration of Reference Pyranometers with Axis Vertical by the Shading Method (Vol. 12.02)
E941-83	Method for Calibration of Reference Pyranometers with Axis Tilted by the Shading Method (Vol. 12.02)
E1109-86	Test Method for Determining the Bulk Density of Solid Waste Fractions (Vol. 11.04)
E1167-87	Guide for Radiation Protection Programs for Decommissioning Operations (Vol. 12.02)
E1188-95	Practice for Collection and Preservation of Information and Physical Items by a Technical Investigator (Vol. 14.02)
E1287-89	Guide for Aseptic Sampling of Biological Materials (Vol. 11.04)
E1370-96	Guide to Air Sampling Strategies for Worker and Workplace Protection (Vol. 11.03)
E1391-94	Guide for Collection, Storage, Characterization, and Manipulation of Sediments for Toxicological Testing (Vol. 11.04)
E1430-91	<i>Guide for Using Release Detection Devices with Underground Storage Tanks (Vol. 11.04); discontinued 2000</i>
E1526-93	<i>Practice for Evaluating the Performance of Release Detection Systems for Underground Storage Tank Systems (Vol. 11.04); discontinued 2002</i>
E1527-00	Practice for Environmental Site Assessments, Phase 1 Environmental Site Assessment Process (Vol. 11.04)

ASTM Standards Indexed in Table B.1 (in Volume 4.08 or 4.09, unless otherwise specified)^a (Continued)

E1528-00	Practice for Environmental Site Assessment Transaction Screen Process (Vol. 11.04)
E1553-93	Practice for the Collection of Airborne Particulate Lead during Abatement and Construction Activities (Vol. 4.07)
E1599-94	Guide for Corrective Action for Petroleum Releases (Vol. 11.04)
E1609-01	Guide for Development and Implementation of a Pollution Prevention Program (Vol. 11.04)
E1689-95	Guide for Developing Conceptual Site Models for Contaminated Sites (Vol. 11.05)
E1739-95	Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites (Vol. 11.04)
E1903-97	Guide for Environmental Site Assessments: Phase II Environmental Site Assessment Process (Vol. 11.04)
E1912-98	Guide for Accelerated Site Characterization for Confirmed or Suspected Petroleum Releases (Vol. 11.04)
E1929-98	Practice for Assessment of Certification Programs for Environmental Professionals: Accreditation Criteria (Vol. 11.04)
E1943-98	Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites (Vol. 11.04)
E1948-98	Guide for Process of Sustainable Brownfields Redevelopment (Vol. 11.04)
E1983-98	Guide for Assessment of Wetland Functions (Vol. 11.04)
E1990-98	Guide for Performing Evaluations of Underground Storage Tank Systems for Operational Conformance with 40 CFR, Part 280 Regulations (Vol. 11.04)
E1991-98	Guide for Environmental Life Cycle Assessment of Building Materials/Products (Vol. 11.04)
E2018-01	Guide for Property Assessments: Baseline Property Condition Assessment Process (Vol. 11.04)
E2081-00	Guide for Risk-Based Corrective Action (Vol. 11.04)
E2091-00	Guide for Use of Activity and Use Limitations, Including Institutional and Engineering Controls (Vol. 11.04)
E2107-00	Practice for Environmental Regulatory Compliance Audits (Vol. 11.04)
E2137-01	Guide for Estimating Monetary Costs and Liabilities for Environmental Matters
E2173-01	Guide for Disclosure of Environmental Liabilities
E2205-02	Guide for Risk-Based Corrective Action for Protection of Ecological Resources
E2247-02	Practice for Environmental Site Assessments: Phase I Environmental Site Assessment Process for Forestland or Rural Property
<i>ES38</i>	<i>Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites; discontinued 1995; replaced by E1739</i>
<i>ES40</i>	<i>Practice for Procedures for the Assessment of Buried Steel Tanks Prior to the Additions of Cathodic Protection (Vol. 11.04); discontinued 1997</i>
F480-99	Specifications for Thermoplastic Water Well Casing Pipe and Couplings Made in Standard Dimension Ratios (SDR) (Vol. 08.04)
F488-95	Test Method for On-Site Screening Heterotrophic Bacteria in Water (Vol. 11.02)
F625-94	Practice for Classifying Water Bodies for Spill Control Systems (Vol. 11.04)
F1084-90	Guide for Sampling Oil/Water Mixtures for Oil Spill Recovery Equipment (Vol. 11.04)
G51-95	Test Method for pH of Soil for Use in Corrosion Testing
G57-95a	Method for Field Measurement of Soil Resistivity Using the Wenner Four-Electrode Method
<i>PS11-95</i>	<i>Practice for Environmental Regulatory Compliance Audits (Vol. 11.04); discontinued 1998; see E2107</i>
<i>PS12-95</i>	<i>Guide for the Study and Evaluation of an Organization's Environmental Management Systems (Vol. 11.04); discontinued 1998</i>
<i>PS14-95</i>	<i>Practice for Lifecycle Costing for Pollution Prevention (Vol. 11.04); discontinued 1998</i>
<i>PS26-96</i>	<i>Guide for Development and Implementation of a Source Reduction Program (Vol. 11.04); discontinued 1998</i>
<i>PS47-95</i>	<i>Test Method for Screening, Quantification, and Characterization of Total Polychlorinated Biphenyls by Room Temperature Phosphorescence (Vol. 11.02); discontinued 1998</i>
<i>PS64-96</i>	<i>Guide for Developing Appropriate Statistical Approaches for Ground-Water Detection Monitoring Programs; discontinued 1998; replaced by D6312</i>
<i>PS78-97</i>	<i>Guide for Selecting Surface Geophysical Methods; discontinued 2000; replaced by D6429</i>
<i>PS85-96</i>	<i>Guide for Expedited Site Characterization of Hazardous Waste Contaminated Sites; discontinued 1998; replaced by D6235</i>
<i>PS104-98</i>	<i>Guide for Risk-Based Corrective Action (Vol. 11.04); discontinued 2000; replaced by E2081</i>

^a Italicized standard designation = discontinued. Prior to 1994, Volume 4.08 contained all standards on soil and rock. Beginning in 1994, this volume was broken into two volumes: Volume 4.08, Soil and Rock (I); and Volume 4.09, Soil and Rock (II); Geosynthetics.

^b The last two digits indicate the year in which the standard was adopted or the most recent year in which substantive revisions to the standard were adopted.

APPENDIX C

Tables and Figures for Estimation of Aquifer Parameters

This appendix contains a series of figures and tables that can be used to estimate vadose zone and aquifer hydrologic properties based on texture of unconsolidated materials and rock type in bedrock aquifers. Refer to Section 7.4.2 for a recommended procedure for estimating porosity, specific yield, and hydraulic conductivity.

Table C.0 provides information to help identify which figures and tables in this appendix can be used based on the type of information known. Worksheet D-W1 can be used to compile estimates for a particular aquifer location.

Table C.0

Figure/Table	Known Properties				Estimated Parameters		
	Grain-Size ^a Distribution	USDA Si-Sa-Cl%	ASTM/ USCS Class	Soil/ Rock Type	Porosity	Specific Yield	Hydraulic Conductivity
Table C.1				x	x		
Table C.2				x		x	
Table C.3			x	x			x
Figure C.1	x				x	x	
Figure C.2		x				x	
Figure C.3				x	x		x
Figure C.4				x			x
Figure C.5				x			x
Figure C.6				x			x
Figure C.7			x	x			x
Figure C.8		x					x
Figure C.9		x + bulk density					x
Figure C.10	x (d ₅₀ , σ_1)			Sands			x
Figure C.11	x (median)			Stratified drift			x
Figure C.12				Glacial till			x
Figure C.13	x + porosity			Sandstone			x
Figure C.14	x	x		Unconsolidated			x
Figure C.15				Unconsolidated ^b		x	x

Note: Si-Sa-Cl% = silt-sand-clay percent.

^a Full grain-size distribution data that allows determination of such characteristics as (1) median grain size, (2) cumulative percent finer than, and (3) standard deviation of grain size. Figure C.14 illustrates a grain-size distribution curve.

^b This figure allows estimation of hydraulic conductivity if specific yield is known or vice versa.

Table C.1 Porosity (% of Volume) of Different Aquifer Materials

Soil/Rock Types	(1) P/S ^a	(2) P/S ^b	(3) ^c	(4)	(5)	(6)	(7) ^d
Unconsolidated Sediments							
Gravel	20/—	30–40/—	23.7–44.1	25–40	25–40		
Coarse						20–35	
Medium						20–35	
Fine						20–40	
Sand and Gravel						20–35	
Sand	25/—		26.0–53.3	25–50	15–48		
Gravelly						20–35	
Coarse		30–40/—				25–45	
Medium						25–45	
Medium to fine		30–35/—					
Fine						25–55	
Dune sand						35–45	
Silt		40–50/yes ^b	33.9–61.1	35–50	35–50	35–60	
Clay	50/–	45–55/yes ^b	34.2–56.9	40–70	40–70	35–55	
Sandy						30–60	
Till		45–55/yes ^b				25–45	
Unstratified drift			22.1–40.6				
Stratified drift			34.6–59.3				
Loess			44.0–57.2			60–80	
Peat						60–80	
Soil	55/–						
Alluvium							10–40 (30)
Basin fill							5–30 (20)
Ogallala formation							15–45 (35)
Consolidated Sediments							
Limestone	10/10	1–50/yes ^b	6.6–55.7	0–20	0–20	5–55	1–20 (4)
Karst				5–50	5–50		
Chalk					5–40		
Dolomite		1–50/yes ^b	19.1–32.7	0–20	0–20		
Sandstone			13.7–49.3	5–30	5–40		1–20 (10)
Semiconsolidated	10/1					1–50	
Coarse, medium		<20/yes ^b					
Fine, argillite		<10/yes ^b					
Siltstone		—/yes ^b	21.2–41.0			20–40	
Shale		—/yes ^b	1.4–9.7	0–10	0–10		
Crystalline Rocks							
Granite (unaltered)	—/0.1				0–2		
Crystalline (fractured)				0–10			
Crystalline (dense)				0–5		0–5	
Igneous/metamorphic		—/yes ^b					
Weathered						40–50	
Unaltered gneiss					0–2		
Quartzite					0–1		
Slates/mica schists					0–10		
Volcanic Rocks							
Basalt	10/1	—/yes ^b					
Fractured				5–50	5–50	5–50	
Volcanic tuff					30–40	10–40	
Acid volcanic rocks		—					

^a P = primary porosity; S = secondary porosity.^b Rarely exceeds 10%.^c Compiled by Barton et al. (1985).^d Number in parentheses is typical value.

Sources: (1) Heath (1983); (2) Brown et al. (1983); (3) Morris and Johnson (1967), compiled by Barton et al. (1985); (4) Freeze and Cherry (1979); (5) Sevee (1991); (6) Devinny et al. (1990); (7) Wilson (1981). See also Manger (1963).

Table C.2 Specific Yield (%) for Different Aquifer Materials

Soil/Rock Types	(1)	(2) Mean	(2) Range	(3)	(4)	(5)
Unconsolidated Sediments						
Gravel	19			15–30		
Coarse		21	13–25		10–25	
Medium		24	17–44		15–25	
Fine		18	13–28		15–35	
Sand and Gravel				15–25	15–30	
Sand	22			10–30		
Gravelly					20–35	
Coarse		30	18–43		20–35	
Medium		32	16–46		15–30	
Fine		33	1–46		10–30	
Dune sand		38	32–47		30–40	
Silt		20	1–39		1–30	
Loess		18	14–22		30–50	
Clay	2	6	1–18	1–10	1–20	
Sandy					1–30	
Till					5–20	
Peat					30–50	
Soil	40					
Alluvium						1–25 (15)
Basin fill						1–30 (15)
Ogallala formation						1–30 (20)
Consolidated Sediments						
Limestone/Carbonate	18	14	0–36	0.5–5	1–24	1–5 (2)
Sandstone				5–15		
Semiconsolidated	6				1–48	0.1–5 (1)
Medium		27	12–41			
Fine		21	2–40			
Siltstone		12	1–33		1–35	
Shale				0.5–5		
Volcanic Rocks						
Basalt	8					
Fractured					1–30	
Tuff		21	2–47		2–35	
Crystalline Rocks						
Granite	0.09					
Schist		26	22–33			
Crystalline (dense)					0–2	
Igneous/metamorphic weathered					20–30	

Sources: (1) Heath (1983); (2) Morris and Johnson (1967), as compiled by McWhorter and Sunada (1977); (3) Sevee (1991); (4) Devinnny et al. (1990); (5) Wilson (1981).

Table C.3 Representative Values for Hydraulic Conductivity of Unconsolidated and Consolidated Sediments

Rock/Soil Type		Hydraulic Conductivity (cm/sec)
Unconsolidated Materials^a		
Gravel (repacked)		$3.1 \text{ to } 3.4 \times 10^{-2}$
Sand		$9.0 \times 10^{-2} \text{ to } 4.7 \times 10^{-6}$
Silt		$7.1 \times 10^{-3} \text{ to } 9.4 \times 10^{-9}$
Clay		$1.4 \times 10^{-6} \text{ to } 1.4 \times 10^{-9}$
Unstratified drift		$1.0 \times 10^{-2} \text{ to } 3.8 \times 10^{-9}$
Stratified drift		$6.6 \times 10^{-1} \text{ to } 4.7 \times 10^{-5}$
Loess		$1.8 \times 10^{-4} \text{ to } 4.7 \times 10^{-6}$
Sedimentary Rocks^a		
Sandstone		$1.0 \times 10^{-2} \text{ to } 3.7 \times 10^{-7}$
Siltstone		$1.4 \times 10^{-6} \text{ to } 9.4 \times 10^{-10}$
Shale		—
Limestone		$2.6 \times 10^{-2} \text{ to } 1.0 \times 10^{-8}$
Dolomite		$3.3 \times 10^{-6} \text{ to } 3.8 \times 10^{-9}$
Unified Soil Classification (when compacted)^b		
GW	Well-graded gravels, gravel–sand mixtures, little or no fines	10^{-2}
GP	Poorly graded gravels, gravel–sand mixtures, little or no fines	10^{-2}
GM	Silty gravels, gravel–sand–silt mixtures	$10^{-3} \text{ to } 10^{-6}$
GC	Clayey gravels, gravel–sand–clay mixtures	$10^{-6} \text{ to } 10^{-8}$
SW	Well-graded sands, gravelly sand, little or no fines	10^{-3}
SP	Poorly graded sands, gravelly sands, little or no fines	10^{-3}
SM	Silty sands, sand–silt mixtures	$10^{-3} \text{ to } 10^{-6}$
SC	Clayey sands, sand–clay mixtures	$10^{-6} \text{ to } 10^{-8}$
ML	Inorganic silts and fine sands, silty or clayey fine sands or clayey silts with slight plasticity	$10^{-3} \text{ to } 10^{-6}$
CL	Inorganic clays of low to medium plasticity, gravelly clays, sandy clays, silty clays, lean clays	$10^{-6} \text{ to } 10^{-8}$
OL	Organic silts and organic silty clays of low plasticity	$10^{-4} \text{ to } 10^{-6}$
MH	Inorganic silts, micaceous or diatomaceous fine sandy or silty soils, elastic silts	$10^{-4} \text{ to } 10^{-6}$
CH	Inorganic clays of high plasticity, fat clays	$10^{-6} \text{ to } 10^{-8}$
OH	Organic clays of medium to high plasticity, organic silts	$10^{-6} \text{ to } 10^{-8}$
Pt	Peat and other highly organic soils	Not classified

^a Compiled from Morris and Johnson (1967) by Barton et al. (1985).

^b Compiled by Brown et al. (1991) from SCS (1990).

Section C.1 discusses use of empirical equations for estimating hydraulic conductivity from grain-size characteristics, and [Section C.2](#) includes empirical equations for estimating scale-dependent hydrodynamic dispersivity in permeable aquifers.

C.1 ESTIMATING SATURATED HYDRAULIC CONDUCTIVITY FROM GRAIN-SIZE CHARACTERISTICS

To use the nomograph in [Figure C.10](#), a particle-size distribution curve, as illustrated in [Figure C.10a](#), must be plotted using ρ units, where $\rho = -\log_2 d$, d being the grain-size diameter in millimeters. The *inclusive standard deviation* must also be calculated as follows:

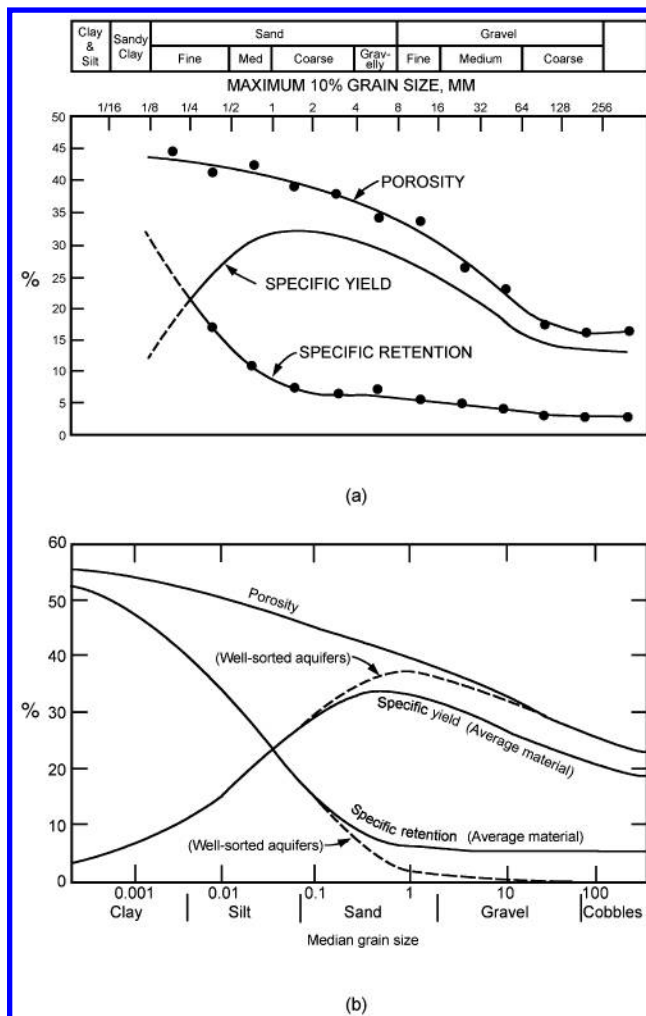


Figure C.1 Porosity, specific yield, and specific retention: (a) mean curves for South Coastal Basin in the Los Angeles area (adapted from Todd, 1959, by Devinnny et al., 1990); (b) alluvium from large valleys (Davis and DeWiest, 1966, using various sources).

$$\sigma_l = (d_{16} - d_{84})/4 + (d_5 - d_{95})/6.6$$

where the subscripts for d (in ρ units) represent the cumulative percentage finer than that diameter.

Figure C.10 provides an illustrative example. Median grain-size d_{50} is first determined from the particle-size curve, C.10a (2.0 in the example). The inclusive standard deviation (calculated from the data used to plot the curve) in the example (0.8) has been interpolated between the curves in the nomograph on the right, C.10b, yielding an approximate K of 0.7 cm/min.

Definitions of terms in the equations in Figure C.14 include D50 = median diameter, in millimeters; D10 = diameter, in millimeters, at which 10% of the sample is finer; Dm = mean diameter, in millimeters; σ_ϕ = phi standard deviation; %sa = percentage of the sample coarser than 0.05 mm; and %cl = percentage of the total sample finer than 0.002 mm.

Citations for the five empirical equations in Figure C.14 are Bedinger (1961), Cosby et al. (1984), Hazen (1893), Krumbein and Monk (1942), and Puckett et al. (1985). An especially useful

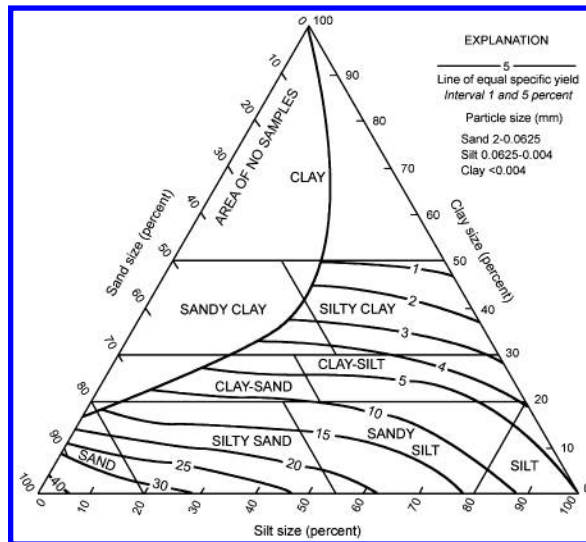


Figure C.2 Textural classification triangle for unconsolidated materials showing the relation between particle size and specific yield (Morris and Johnson, 1967).

Rock types	Porosity		Permeability range (cm/sec)						Well yields			Type of water-bearing unit	
	Primary (grain)	Secondary (fracture) ¹	10 ²	10 ⁰	10 ⁻²	10 ⁻⁴	10 ⁻⁶	10 ⁻⁸	High	Medium	Low		
Sediments, unconsolidated													
Gravel	30-40		_____						_____			Aquifer	
Coarse sand	30-40			_____					_____			Aquifer	
Medium to fine sand	30-35			_____					_____			Aquifer	
Silt	40-50	Occasional				_____					_____	Aquiclude	
Clay, till	45-55	Rare (mud cracks)					_____				_____	Aquiclude	
Sediments, consolidated													
Limestone, dolomite	1-50	Solution joints, planes	_____						_____			Aquifer or aquifuge	
Coarse, medium sandstone	< 20	Joints and fractures	_____						_____			Aquifer or aquiclude	
Fine sandstone, argillite	< 10	Joints and fractures			_____						_____	Aquifer or aquifuge	
Shale, siltstone	—	Joints and fractures				_____					_____	Aquifuge or aquifer	
Volcanic rocks													
Basalt	—	Joints, fractures	_____						_____			Aquifer or aquifuge	
Acid volcanic rocks	—					_____					_____	Aquifuge or aquifer	
Crystalline rocks													
Plutonic and metamorphic		Weathering and fractures decreasing as depth increases			_____						_____	Aquifuge or aquifer	

1. Rarely exceeds 10 %

Figure C.3 Porosity, permeability, and well yields of major rock types (Brown et al., 1983)

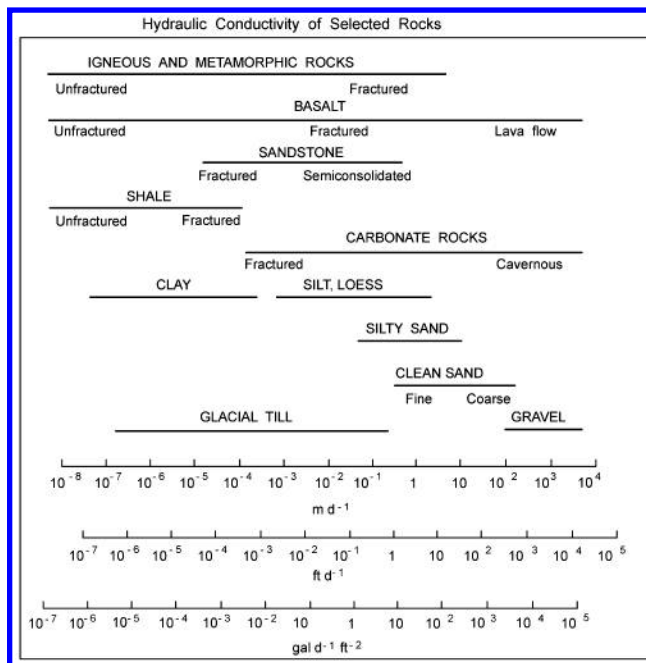


Figure C.4 Hydraulic conductivity of selected rocks (Heath, 1983).

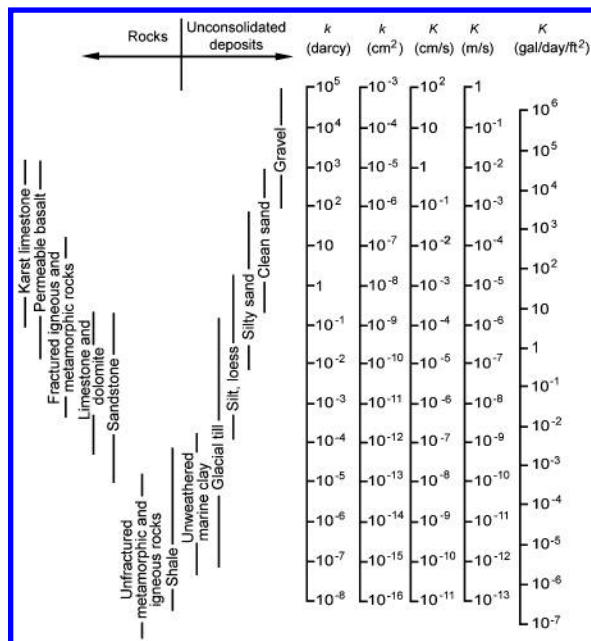


Figure C.5 Range of values of hydraulic conductivity (after Freeze and Cherry, 1979).

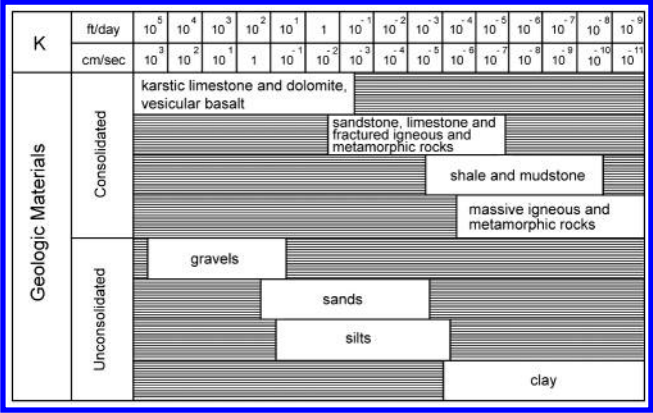


Figure C.6 Representative ranges of saturated hydraulic conductivity values for geologic materials (adapted from Freeze and Cherry, 1979, by Thompson et al., 1989).

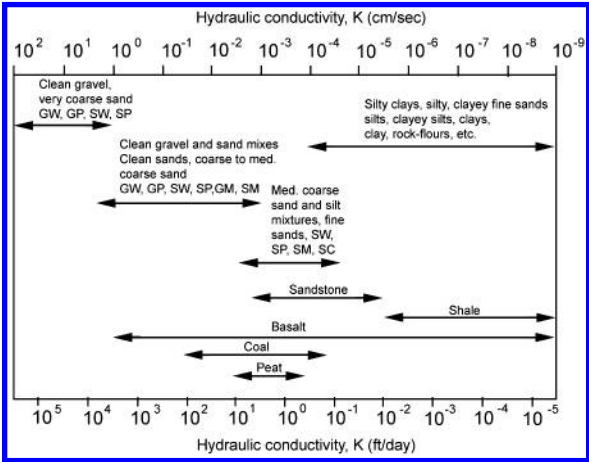


Figure C.7 Typical values of soil and rock hydraulic conductivity (Dawson and Istok, 1991, after Bowles, 1984, and Walton, 1987).

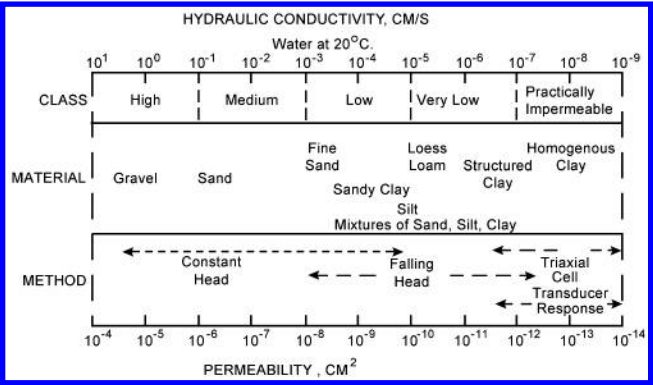


Figure C.8 Saturated hydraulic conductivity of unconsolidated materials (Klute and Dirksen, 1986).

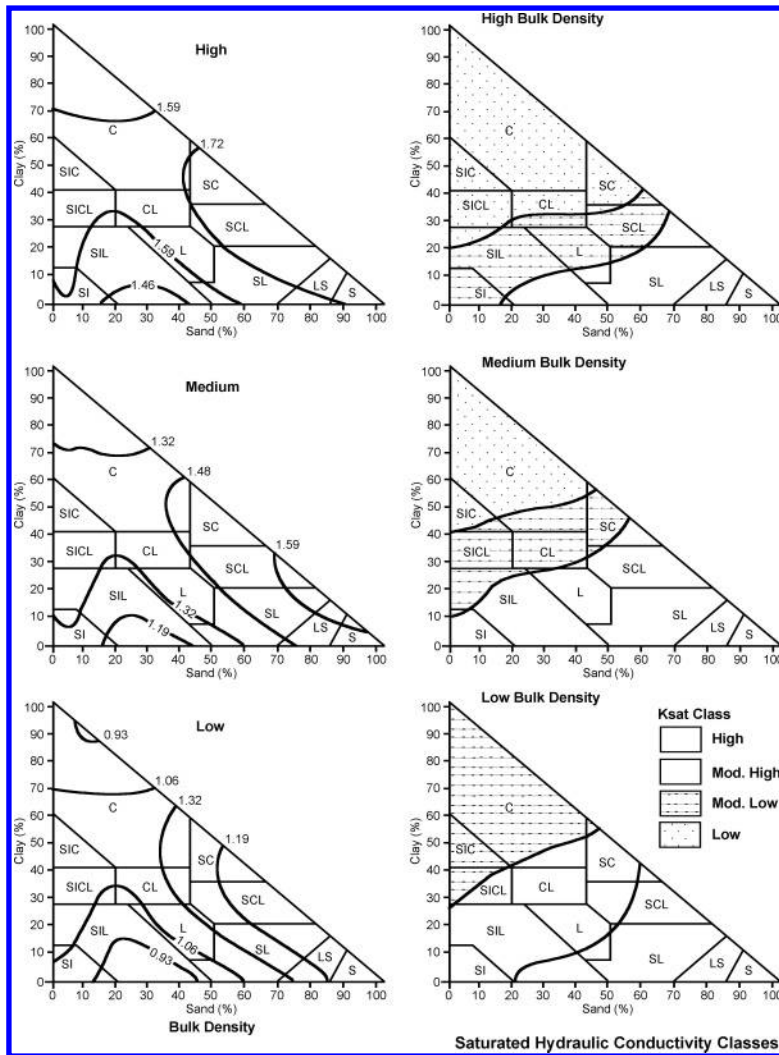


Figure C.9 Estimation of hydraulic conductivity from USDA texture and bulk density: determine bulk density class and then Ksat class (refer to Table C.4 for class ranges).

empirical equation for estimating hydraulic conductivity is that developed by Zhang and Brusseau (1998) using the ASTM/USCS grain-size classification system:

$$\log_{10}k_{(cm/sec)} = 1.854 - 9.640 \times 10^{-2}(\text{clay}\%) - 5.936 \times 10^{-1}(\text{silt}\%)^{0.5} - 3.478 \times 10^{-2}(\text{sand}\%) - 4.196 \times 10^{-1}(\text{gravel}\%)^{0.5}$$

This formula was developed using data from 29 samples from an alluvial aquifer near Tucson, AZ. Measured hydraulic conductivities varied over four orders of magnitude and represent a wide range of mixtures of gravel (63% maximum), sand (82% maximum), silt (64% maximum), and clay (25% maximum). The resulting nonlinear regression equation is probably applicable to a wider range of materials than any other available equation.

Other references that contain empirical equations for estimating hydraulic conductivity include Alyamani and Sen (1993), Hendry and Paterson (1982), Horn (1971), Uma et al. (1989), Vukovic and Soro (1992), and Wiebenga et al. (1970). Empirical equations should only be used when

Table C.4 SCS Criteria for Hydraulic Conductivity Classes

Class	μ/sec	in./h
Very low (VL)	<0.01	<0.001
Low (L)	0.01–0.1	0.001–0.01
Moderately low (ML)	0.1–1	0.01–0.14
Moderately high (MH)	1–10	0.14–1.4
High (H)	10–100	1.4–14.2
Very high (VH)	>100	>14.2

Source: Boulding (1991).

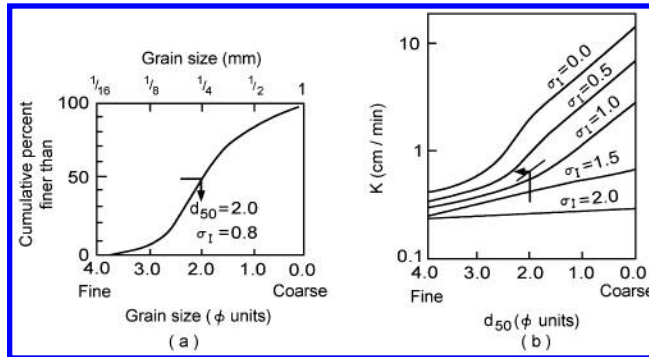


Figure C.10 Determination of grain-size gradation curves for sands (Freeze and Cherry, 1979, after Masch and Denny, 1966).

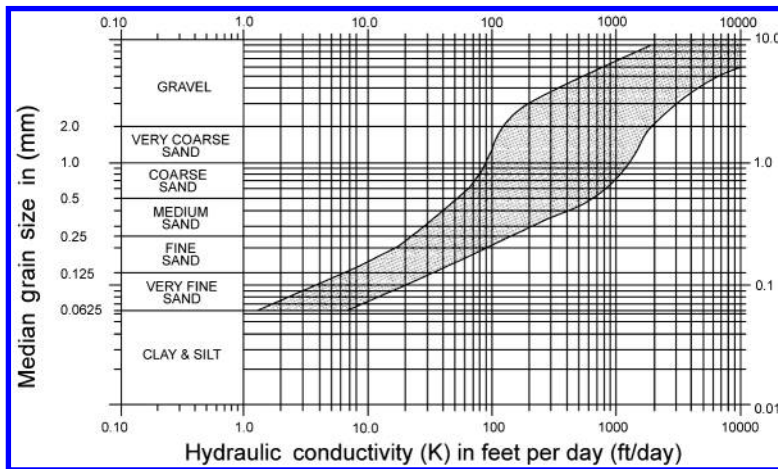


Figure C.11 Relationship between grain size and hydraulic conductivity in stratified drift aquifers (Connecticut Department of Environmental Protection, 1991).

materials being evaluated have textural or geologic characteristics similar to materials from which the equations were derived (see reference annotations).

C.2 ESTIMATING SCALE-DEPENDENT HYDRODYNAMIC DISPERSIVITY

Hydrodynamic dispersion causes contaminants to move more rapidly through an aquifer than would be expected based in simple ground water velocity (Section 4.4.2). The Electric Power Research Institute (EPRI, 1994), based on the work of Gelhar et al. (1992), has developed several

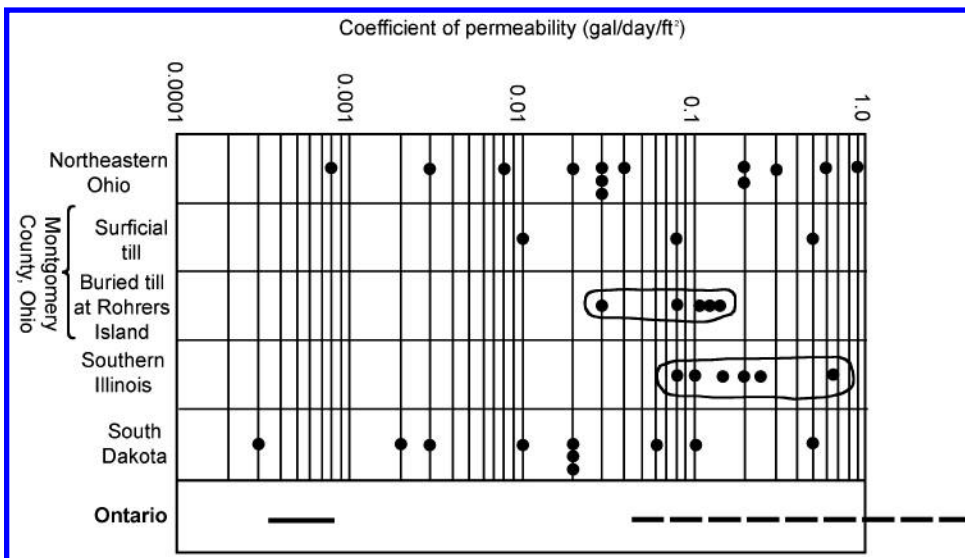


Figure C.12 Range of permeability of glacial tills: \bullet = laboratory measurements (Norris, 1963); circled clusters of dots based on pumping tests (Norris, 1963); Ontario data from McKay et al. (1993) with solid line indicating range of laboratory measurements and dashed line the range of mean values using four different types of piezometer construction for field measurements.

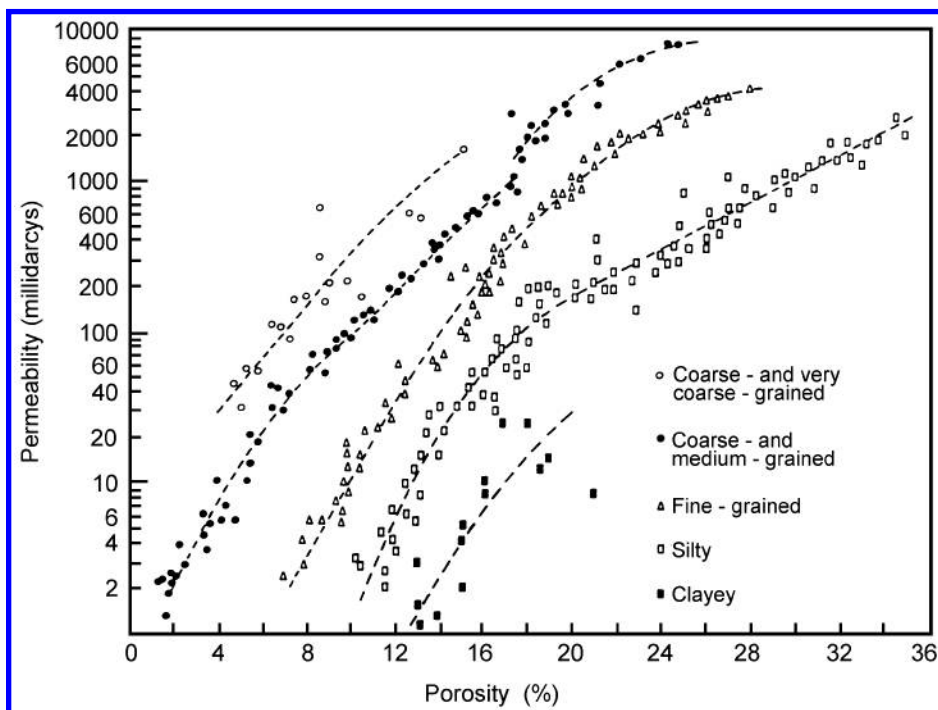


Figure C.13 Relationship between porosity and permeability for sandstone in various grain-size categories (Freeze and Cherry, 1979, after Chilingar, 1963).

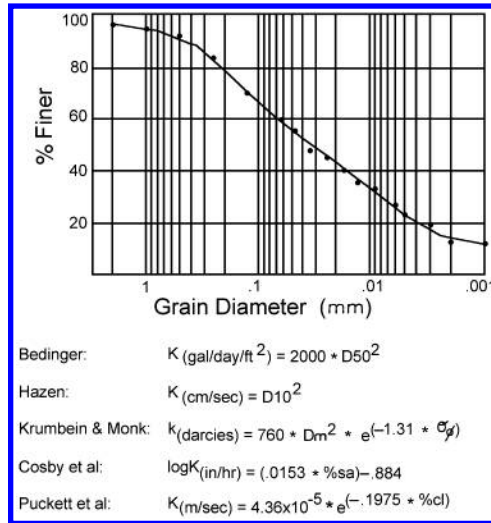


Figure C.14 Sample particle-size distribution curve and five empirical equations used to estimate hydraulic conductivity of unconsolidated materials (Bradbury and Muldoon, 1990).

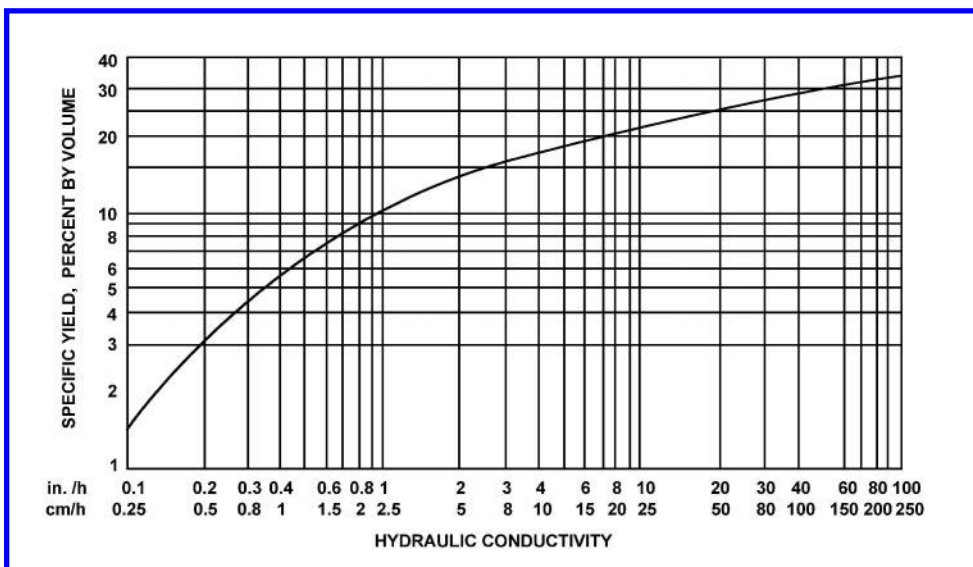


Figure C.15 General relationship between specific yield and hydraulic conductivity (Bureau of Reclamation, 1978).

empirical equations for estimating hydrodynamic dispersivity of contaminant plumes. Contaminant plumes can disperse *longitudinally* (in the direction of ground water flow) and *laterally* in a vertical and horizontal direction. The equations for longitudinal dispersivity, α_l , for different permeable aquifer materials are as follows (where x = distance downgradient from the contaminant source in meters):

$$\text{Sand: } \alpha_l = 4.3485 \times 10^{-3} (x)^{1.0466}$$

$$\text{Sand and gravel: } \alpha_l = 3.4604 \times 10^{-2} (x)^{0.73963}$$

$$\text{Gravel: } \alpha_l = 0.1 (x)^{0.57597}$$

$$\text{Fractured rock: } \alpha_l = 0.2 (x)^{0.56632}$$

EPRI (1994) suggests an average transverse horizontal dispersivity for all materials, based on ratios of α_{th}/α_l as

$$\alpha_{th} = 0.28 \alpha_l$$

Transverse vertical dispersivities for the different materials are as follows:

$$\text{Sand: } \alpha_{tv} = 0.069 \alpha_l$$

$$\text{Sand and gravel: } \alpha_{tv} = 0.048 \alpha_l$$

$$\text{Gravel: } \alpha_{tv} = 0.026 \alpha_l$$

$$\text{Fractured rock: } \alpha_{tv} = 0.1 \alpha_l$$

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* See Preface for information on how to obtain documents.

APPENDIX D

Worksheets and Checklists for Ground Water and Wellhead Protection

This appendix contains a series of worksheets and checklists to assist in hydrogeologic characterization, with a focus on applications for delineating and managing wellhead protection areas. The first six checklists can be used to assist in hydrogeologic mapping, selection of simple analytical equations or computer models for delineation of wellhead protection areas, and vulnerability mapping using the DRASTIC system. Worksheets D-W7 through D-W11 and Checklists D-C1 through D-C5 are intended to be used for identification of potential contaminant sources within an area of interest. Section 11.3.1 provides a step-by-step procedure for conducting a potential contaminant source inventory. Checklists D-C6 and D-C7 can be used to help assist the relative risk posed by potential contaminant sources and to identify potential management practices to prevent or minimize ground-water contamination. The following provides an easy reference to worksheets and checklists in this appendix:

	Worksheets for Hydrogeologic Characterization	Page
D-W1	Water Well/Aquifer Data	
D-W2	Collection of Existing Data for Wellhead Protection	
D-W3	Possible Aquifer Boundaries	
D-W4	Aquifer Characteristics for the Selection of Analytical Solutions to Ground Water Flow in the Vicinity of Wells	
D-W5	Ground Water Computer Code Specifications and Code Suitability for a Specific Site	
D-W6	DRASTIC Evaluation	
	Worksheets for Contaminant Source Inventories	
D-W7	Residential Potential Contaminant Source Inventory	
D-W8	Farm Potential Contaminant Source Inventory	
D-W9	Transportation Hazard Inventory	
D-W10	Municipal/Commercial/Industrial Potential Contaminant Source Inventory: Short Form	
D-W11	Municipal/Commercial/Industrial Potential Contaminant Source Inventory: Long Form	
	Checklists for Contaminant Source Inventories	
D-C1	Potential Contaminant Source Short List for Wellhead Protection	
D-C2	Cross-Cutting Potential Contaminant Sources	
D-C3	Nonindustrial Potential Contaminant Sources	
D-C4	Potential Contaminant Sources: Commercial, Natural Products Processing/Storage, and Resource Extraction	
D-C5	Potential Industrial Contaminant Sources	
	Checklists for Risk Assessment and Ground-Water Protection Options	
D-C6	Risk Categories of Land Uses and Activities Affecting Ground-Water Quality	
D-C7	Wellhead Protection Tools	

Worksheet D-W1

Water Well/Aquifer Data

Well Data (attach drillers log):

Location _____

Screen interval depth _____

Water level data:

Date _____

Level (ft) _____

Pumping Characteristics:

Current nonpumping water level (ft below ground surface) _____

Current pumping rate (gpm) _____

Typical pumping duration (h/day) _____

Current pumping water level (ft below ground surface) _____

Typical nonpumping duration (h/day) _____

Estimated annual pumpage (pumping rate \times h/day \times 365 \times 60) = _____

Specific capacity (pumping rate/(nonpumping water level minus pumping water level)) = _____ gpm/ft drawdown^a

Estimated transmissivity (specific capacity \times 2000) = _____ gpd/ft^a

Estimated hydraulic conductivity (transmissivity/aquifer thickness) = _____ gpd/ft^{2a}

Aquifer Material:		Porosity (%)	K_{sat}^b (_____)	Specific Yield (%)
Unconsolidated Sediments	Low	_____	_____	_____
___ Gravel				
___ Coarse sand	Average	_____	_____	_____
___ Medium to fine sand				
___ Silt	High	_____	_____	_____
___ Clay, till				
Consolidated Sediments	Sources:			
___ Limestone, dolomite	Table(s)	_____	_____	_____
___ Coarse, medium sandstone				
___ Fine sandstone	Figure(s)	_____	_____	_____
___ Shale, siltstone				
Volcanic rocks				
___ Basalt				
___ Acid volcanic rocks				
Crystalline Rocks				
___ Granite/gabbro				
___ Metamorphic				

Aquifer Classification:

Unconfined	Confined	Number of Aquifers
___ Perched	___ Semiconfined	___ One
___ Regional	___ Highly confined	___ Two
		___ > Two (# _____)

Aquifer Boundaries:

Recharge Boundaries

___ Interfluv
___ Losing stream
___ Lake, pond
___ Sinkholes (karst)
___ Injection well
___ Ground-Water Divide

Discharge Boundaries

___ Artesian/pumping well
___ Gaining stream
___ Drainage ditch
___ Tile drains
___ Springs
___ Lakes, ponds
___ Semiconfined aquifer leakage

Worksheet D-W1 (*Continued*)

Expected Water Level Fluctuations (see Table 2.3):

Moisture Regime

- ☐ High moisture (H)^c
- ☐ Moderate moisture (M)
- ☐ Low moisture (L)

Zone of Aeration (d)

- ☐ d < 0.5 m (H)^c
- ☐ d = 0.5–4 m (M)
- ☐ d > 4 m (L)

Diurnal/Intermittent Fluctuations

- ☐ Evapotranspiration
- ☐ Tidal effects near ocean
- ☐ Atmospheric pressure effects

Seasonal Fluctuations

- ☐ Ground-water recharge area
- ☐ Stream bank storage effects

Drainage/Slope

- ☐ Well developed/steep (H)^c
- ☐ Moderate/upland (M)
- ☐ Poor/flat, bottoms (L)

Long-Term Fluctuations

- ☐ Ground-water pumpage
- ☐ Deep-well injection
- ☐ Artificial recharge
- ☐ Pond, lagoon, landfill leakage
- ☐ Agricultural irrigation
- ☐ Agricultural drainage
- ☐ Geotechnical drainage (open pit mines, slopes, tunnels)

^a See Section 7.4.3 for additional discussion of this simple well test for estimating hydraulic conductivity.

^b Saturated hydraulic conductivity (specify units).

^c Rating for expected degree of fluctuation: H = high, M = moderate, L = low.

Worksheet D-W2

Collection of Existing Data for Wellhead Protection

Contacts and Phone Numbers

EPA Regional Ground-Water Representative: _____

USGS Water Resources Division State Office: _____

SCS District/State Office: _____

Federal Management Agency Local Office^a: _____

State Wellhead Protection Program: _____

State Water Resource Agency^b: _____

State Environmental Protection Agency^b: _____

State Geological Survey: _____

Local College/University Geology Department: _____

Local College/University Library: _____

Topographic Maps

___ 7 1/2' topographic

___ 15' topographic

___ Regional

___ Other

Soils/Vegetation Maps

___ Soil map

___ Vegetation

Geologic Maps

___ State

___ Regional

___ Local

Aerial Photography

___ Large scale

___ High altitude

___ Satellite

Hydrologic Maps

___ USGS Hydrologic Atlas

___ State-published hydrologic maps

___ Water table/potentiometric surface

___ Watershed

___ Wetlands

___ Flood plain maps (FEMA, FIRM)

___ Other

Land Use Maps

___ Ownership/tax assessment

___ Subsurface ownership (if different from surface ownership)

___ Zoning/planning

___ Utilities

___ Other

^a Required only if wellhead protection area includes federal lands (most likely in western U.S.). Possible agencies include the Bureau of Land Management, U.S. Forest Service, U.S. Fish and Wildlife Service, and U.S. Department of Defense.

^b If different from agency responsible for wellhead protection.

Worksheet D-W3

Possible Aquifer Boundaries

<u>Barrier Boundaries</u>	Distance to well	Within ZOC? ^a	
		Yes	No
___ Vertical/sloping			
___ Impermeable crystalline rocks	_____	_____	_____
___ Fault displacement	_____	_____	_____
___ Horizontal ^b			
<u>Recharge Boundaries</u>			
___ Natural ground-water divide (unconfined aquifer)	_____	_____	_____
___ Areal recharge from precipitation	_____	_____	_____
___ Loosing stream	_____	_____	_____
___ Lake, other surface water body			
___ Above water table	_____	_____	_____
___ Surface expression of water table	_____	_____	_____
___ Leaky confining layer (downward flow)	_____	_____	_____
___ Injection well	_____	_____	_____
___ Areal artificial recharge	_____	_____	_____
<u>Discharge Boundaries</u>			
___ Gaining stream	_____	_____	_____
___ Lake, other surface water body			
___ Surface expression of water table	_____	_____	_____
___ Interior drainage basin	_____	_____	_____
___ Spring(s)	_____	_____	_____
___ Karst conduit flow	_____	_____	_____
___ Leaky confining layer (upward flow)	_____	_____	_____
___ Drainage ditch/tile drain	_____	_____	_____
___ Other pumping wells	_____	_____	_____

^a As defined by one or more of the simple methods described in Section 11.2.2.

^b Impermeable geologic materials always form the base of an aquifer; see Table 7.4 for criteria for defining the extent to which impermeable confining layers represent boundaries to flow.

Worksheet D-W4

Aquifer Characteristics for the Selection of Analytical Solutions to Ground Water Flow in the Vicinity of Wells

Aquifer Type

- ☐ Water table/unconfined
- ☐ Confined, leaky
- ☐ Confined, nonleaky

Regional Hydraulic Gradient

- ☐ <0.0005 (nearly flat)
- ☐ 0.0005–0.001 (transitional)
- ☐ >0.001 (sloping)

Number of Aquifers

- ☐ One
- ☐ Two
- ☐ More than two

Well Penetration

- ☐ Fully penetrating well
- ☐ Partially penetrating well

Aquifer Properties

- ☐ Porous media
- ☐ Fracture flow^a
- ☐ Karst conduit flow
- ☐ Isotropic
- ☐ Anisotropic
- ☐ Homogeneous hydraulic parameters
- ☐ Heterogeneous hydraulic parameters^a

Flow Character/Dimension

- ☐ Steady-state
- ☐ Transient
- ☐ Radial
- ☐ X
- ☐ X-Y
- ☐ X-Y-Z

^a Analytical solutions are not able to handle fracture flow or heterogeneous aquifer properties. In this situation, maximum measured or estimated aquifer parameters such as porosity and hydraulic conductivity should be used to account for reduced time of travel resulting from fracture flow and hydrodynamic dispersion caused by localized areas of higher hydraulic conductivity.

Worksheet D-W5

Ground Water Computer Code Specifications and Code Suitability for a Specific Site

Model Name: _____ IGWMC No.: _____
Contact: _____ Available from: _____ IGWMC
Address: _____ Other Location _____

Phone: _____

Site/Model Characteristics	Model System Requirements	Computer Match Requirements?	
		Yes	No
_____ Unconfined (water table)	_____ IBM PC/AT/XT (circle)	_____	_____
_____ Semiconfined (leaky)	_____ Other computer _____	_____	_____
_____ Confined	<u>Random Access Memory</u>		
_____ Single aquifer	_____ 640 K	_____	_____
_____ Multiple aquifers	_____ 4 MB	_____	_____
_____ Isotropic	_____ Other (_____)	_____	_____
_____ Homogeneous	<u>Disk Drives</u>		
_____ Anisotropic	_____ Single floppy (HD _____, DD _____)	_____	_____
_____ Heterogeneous	_____ Two floppy (HD _____, DD _____)	_____	_____
_____ Radial	_____ Hard drive	_____	_____
_____ One-dimensional	<u>Disk Operating System</u>		
_____ Two-dimensional	_____ DOS 2.1	_____	_____
_____ Three-dimensional	_____ >DOS 2.1 (_____)	_____	_____
_____ Steady flow	<u>Math Coprocessor</u>		
_____ Transient flow	_____ Required	_____	_____
_____ Variably saturated flow	_____ Optional	_____	_____
_____ Single-phase flow	<u>Graphics</u>		
_____ Multiphase flow	_____ CGA	_____	_____
_____ Hydrodynamic dispersion	_____ EGA	_____	_____
_____ Retardation	_____ VGA	_____	_____
_____ Decay/degradation			

Boundary Conditions: See Worksheet D-W3

Site/Model Output

_____ Zone of influence
_____ Cone of depression
_____ Time of travel
_____ Velocity
_____ Pathways
_____ Zone of contribution
_____ Fluxes
_____ Concentration

Usability^a

Yes No ?

_____ Preprocessor
_____ Postprocessor
_____ User's instructions
_____ Sample problems
_____ Hardware dependency
_____ Support

Reliability^a

Yes No ?

_____ Theory peer reviewed
_____ Coding peer reviewed
_____ Verified
_____ Field validation

Model Users: _____ Many _____ Few _____ Unknown

^a Information on usability and reliability for most currently available models can be found in appendix tables in van der Heijde and Einawawy (1993).

Worksheet D-W6

DRASTIC Evaluation (Circle appropriate range and rating)

County: _____ State: _____

General Soil Map Unit Number: _____ General Description: _____

1. Depth to Water (ft) 2. Net Recharge (in.) 3. Aquifer Media

Range	Rating	Range	Rating	Type	Range	Rating Typical	Actual
0–5	10	0–2	1	Massive shale	1–3	2	_____
5–15	9	2–4	3	Metamorphic/igneous	2–5	3	_____
15–30	7	4–7	6	Weathered M/I	3–5	4	_____
30–50	5	7–10	8	Glacial till	4–6	5	_____
50–75	3	10+	9	Bedded SS/LS/shale	5–9	6	_____
75–100	2			Massive sandstone	4–9	6	_____
100+	1			Massive limestone	4–9	6	_____
				Sand and gravel	4–9	8	_____
				Basalt	2–10	9	_____
				Karst limestone	9–10	10	_____

4. Soil Media 5. Topography (%) 6. Vadose Zone Media

Type	Rating	Range	Rating	Type	Range	Rating Typical	Actual
Thin/		0–2	10	Confining layer	1	1	_____
Absent	10	2–6	9	Silt/clay	2–6	3	_____
Gravel	10	6–12	5	Shale	2–5	3	_____
Sand	9	12–18	3	Limestone	2–7	6	_____
Peat	8	18+	1	Sandstone	4–8	6	_____
Structured				Bedded LS/SS/shale	4–8	6	_____
clay	7			Sand and gravel with			
Sandy loam	6			Significant silt and clay	4–8	6	_____
Loam	5			Metamorphic/igneous	2–8	4	_____
Silty loam	4			Sand and gravel	6–9	8	_____
Clay loam	3			Basalt	2–10	9	_____
Muck	2			Karst limestone	8–10	10	_____
Massive							
clay	1						

7. Hydraulic Conductivity (gpd/ft²)**DRASTIC Index**

Range	Rating	Rating × Weight =	Pesticide Rating × Weight =
1–100	1	1. _____ × 5 = _____	1. _____ × 5 = _____
100–300	2	2. _____ × 4 = _____	2. _____ × 4 = _____
300–700	4	3. _____ × 3 = _____	3. _____ × 3 = _____
700–1000	6	4. _____ × 2 = _____	4. _____ × 5 = _____
1000–2000	8	5. _____ × 1 = _____	5. _____ × 3 = _____
2000+	10	6. _____ × 5 = _____	6. _____ × 4 = _____
		7. _____ × 3 = _____	7. _____ × 2 = _____
		Total _____ ^a	Total _____ ^a

^a Aquifers with DRASTIC ratings of >150 are considered to be highly vulnerable by the EPA.

Worksheet D-W7 Residential Potential Contaminant Source Inventory (North Dakota State Department of Health)



**WELLHEAD PROTECTION AREA SURVEY FORM
RESIDENTIAL**

DATE: _____
PWS: _____

This survey form is designed to inventory activities that may impact groundwater quality within the public water supply wellhead protection area (WHPA).

Name: _____
Address: _____
City: _____
Phone: _____

Please describe all water wells on the property:

First well:
Use/Name: _____
(e.g., stock, house, irrigation)

Depth: _____ Diameter: _____
Depth to water: _____
Pumping rate (gallons per minute): _____
What year was the well installed? _____
Location: Township _____ Range _____
Section _____ Quarters _____
(Please locate on the section/block map provided.)

Second Well:
Use/Name: _____
(e.g., stock, house, irrigation)

Depth: _____ Diameter: _____
Depth to water: _____ Pumping rate (gallons per minute): _____
What year was the well installed? _____
Location: Township _____ Range _____ Section _____ Quarters _____
(Please locate on the section/block map provided.)

Third Well:
Use/Name: _____
(e.g., stock, house, irrigation)

Depth: _____ Diameter: _____
Depth to water: _____ Pumping rate (gallons per minute): _____
What year was the well installed? _____
Location: Township _____ Range _____ Section _____ Quarters _____
(Please locate on the section/block map provided.)

← 1 mile or 1 block →

SECTION MAP

This map represents an entire section of land. Please take care to plot the location of the source to the nearest 10 acres (see instructions). This map may also be used to represent a one one-block area.

Are there any abandoned wells on the property? _____
If Yes, were they plugged and how? _____

If there is a septic tank/drain field on the property, please describe:

Septic tank:
Location: _____
(township, range, section, quarters, or other description; also locate on map)
Size: _____ Depth: _____ Year: _____ Last pumped out: _____

Drain field size and location: _____

Is there any heating/fuel oil storage on the property? Describe: _____

Are there any livestock on the property? Describe (if farm, please use Farm form): _____

Please describe any chemicals used or stored on the property.
Storage: _____

Usage: (fertilizers or pesticides on lawns or gardens? what type? quantity? frequency?) _____

Disposal: _____

Are there any floor drains in your home or building that do not connect to the city sewer system?
If so, what is disposed of there? _____

Other problems or comments: _____

Worksheet D-W8 Farm Potential Contaminant Source Inventory (North Dakota State Department of Health)



DATE: _____
PWS: _____
WELLHEAD PROTECTION AREA SURVEY FORM
FARM

This survey form is designed to inventory activities that may impact groundwater quality within the wellhead protection area (WHPA).

Name: _____
Address: _____
City: _____
Phone: _____

Please describe all water wells on the property:

First well:
Use/Name: _____
(e.g., stock, house, irrigation)
Depth: _____ Diameter: _____
Depth to water: _____
Pumping rate (gallons per minute): _____
What year was the well installed? _____
Location: Township _____ Range _____
Section _____ Quarters _____
(Please locate on the section/block map provided.)

Second Well:
Use/Name: _____
(e.g., stock, house, irrigation)
Depth: _____ Diameter: _____
Depth to water: _____ Pumping rate
(gallons per minute): _____
What year was the well installed? _____
Location: Township _____ Range _____ Section _____ Quarters _____
(Please locate on the section map provided.)

Third Well:
Use/Name: _____
(e.g., stock, house, irrigation)
Depth: _____ Diameter: _____
Depth to water: _____ Pumping rate (gallons per minute): _____
What year was the well installed? _____
Location: Township _____ Range _____ Section _____ Quarters _____
(Please locate on the section map provided.)

← 1 mile or 1 block →

SECTION MAP
This map represents an entire section of land. Please take care to plot the location of the source to the nearest 10 acres (see instructions). This map may also be used to represent a one one-block area.

Are there any abandoned wells on the property? _____
If yes, were they plugged and how? _____

If there is a septic tank/drain field on the property, please describe:

Septic tank:

Location: _____

(township, range, section, quarters, or other description; also locate on map)

Size: _____ Depth: _____ Year: _____ Last pumped out: _____

Drain field size and location: _____

Is there any heating/fuel oil storage on the property? Describe: _____

Please list the crops that you typically plant. _____

What is the total acreage that you farm? _____

Please list each crop separately followed by the number of acres that are generally in that crop or the percentage of the total in that crop.

Crop #1 _____ acres or % _____

Crop #2 _____ acres or % _____

Crop #3 _____ acres or % _____

Crop #4 _____ acres or % _____

Chemicals (pesticides or fertilizers):

Please list the chemicals that you applied to each crop in the last two years.

<u>Crop#</u>	<u>Chemicals applied</u>	<u># of Years</u>	<u>Volume</u> <u>Kg/hectare/yr</u>
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

Please describe any chemical storage procedures and the name of the chemicals which you currently store. _____

Please describe any irrigation or chemigation practices. _____

Please describe any chemical mixing practices. _____

Please describe your container disposal practices. _____

Are there any livestock on the property? _____

Please list the types of livestock, how many, and their location. _____

Please describe the location, age, and design of any feedlots. _____

Please describe any manure storage on the property. _____

Do you have any underground storage tanks? If so, describe their size, location, and contents. _____

Do you have any above ground storage tanks? If so, describe their size, location, and contents. _____

Other problems or comments: _____

Worksheet D-W9 Transportation Hazard Inventory (Adapted from Ohio Environmental Protection Agency, 1991)

1. Facility name: _____
2. Facility type: _____ Railroad _____ Highway _____ Sewer _____ Fuel/chemical pipeline _____
Terminal _____ Service area _____ Other: _____
3. Location: _____

4. Map No.: _____
5. Minimum distance from nearest public well: _____
6. Potential pollution sources (operation and construction information): _____

7. Describe any past pollution incidents: _____

8. Date of installation (pipelines): _____
9. Additional information (protection measures, handling practices, etc.):

Worksheet D-W10 Municipal/Commercial/Industrial Potential Contaminant Source Inventory: Short Form
(Adapted from Adams et al., 1992)

1a. Facility name: _____ 1b. Facility Map Location Number: _____

2. Facility address: _____

3. Owner/operator/other: _____

4. Type of business/facility: _____

5. Type of hazard observed: _____

6. Are storage tanks present? _____ Yes _____ No (If no, skip to question 7)

If yes, are the tanks aboveground (AG)? _____ Below ground (BG)? _____

If yes, is secondary containment present: _____ Yes _____ No

	<u>Age</u>	<u>Size</u>	<u>Tank Material</u>	<u>Material Stored</u>	<u>AG/BG</u>
Tank 1					
Tank 2					
Tank 3					
Tank 4					
Tank 5					
Tank 6					
Tank 7					
Tank 8					
Tank 9					
Tank 10					

Comments: _____

7. Are solvents present? _____ Yes _____ No (If no, skip to question 8)

	<u>Type</u>	<u>Storage Method</u>	<u>Quantity Stored</u>	<u>Disposal Method</u>	<u>Use</u>
Solvent 1					
Solvent 2					
Solvent 3					
Solvent 4					
Solvent 5					

Comments: _____

8. Is the facility sewer? _____ Yes _____ No

If yes, are any floor drains connected to the sewer? _____ Yes _____ No

If no, describe wastewater disposal methods: _____

Comments: _____

9. Is the facility subject to an environmental remediation? _____ Yes _____ No (If no, skip to question 10)

If yes, what type of remediation?

Is this remediation currently under agency litigation, voluntary cleanup, other?

Comments:

10. Are there any physical observations that may indicate a potential hazard to the ground water? _____ Yes
_____ No (If no, skip to question 11)

If yes, describe:

Comments:

11. Summarize the results of the findings enumerated above, and indicate the degree of potential hazard this facility may pose to ground water.

Inspector: _____

Date inspected: _____

**Worksheet D-W11 Municipal/Commercial/Industrial Potential Contaminant Source Inventory: Long Form
(Adapted from Adams et al., 1992)**

1. Unique ID number:

Distance and direction from wellhead:

2. Type of business/facility:

3. Does the facility operate under any permits issued by a state or federal regulatory agency? _____ Yes
_____ No If yes, provide the following information:

Issuing Agency

Permit Number

Type of Permit

Permit 1

Permit 2

Permit 3

Permit 4

Permit 5

Comments:

Does the facility have any history of noncompliance with permit terms? _____ Yes _____ No If yes, provide the following information:

Date

Type of Violation

Disposition

Violation 1

Violation 2

Violation 3

Violation 4

Violation 5

Comments:

4. Does the facility have a ground-water monitoring system? _____ Yes _____ No If yes, describe:

Have any ground-water samples exceeded compliance requirements or shown evidence of contamination?
_____ Yes _____ No If yes, describe:

Comments:

5. Are storage tanks present? _____ Yes _____ No (If no, skip to question 7)

If yes, are the tanks above ground (AG) _____? Below ground (BG) _____?

If yes, is secondary containment present: _____ Yes _____ No

Age

Size

Tank Material

Material Stored

AG/BG

Tank 1

Tank 2

Tank 3

Tank 4
Tank 5
Tank 6
Tank 7
Tank 8
Tank 9
Tank 10

Comments:

6. Are solvents present? _____ Yes _____ No (If no, skip to question 8)

	<u>Type</u>	<u>Storage Method</u>	<u>Quantity Stored</u>	<u>Disposal Method</u>	<u>Use</u>
Solvent 1					
Solvent 2					
Solvent 3					
Solvent 4					
Solvent 5					

Comments:

7. Is the facility sewer? _____ Yes _____ No

If yes, are any floor drains connected to the sewer? _____ Yes _____ No

If no, describe wastewater disposal methods:

8. Has on-site past or present landfilling, land treating, or surface impoundment of waste, other than landscape waste or construction and demolition debris, occurred? _____ Yes _____ No If yes, describe:

9. Are there currently any on-site piles of special or hazardous waste? _____ Yes _____ No

If yes, describe:

10. Are on-site piles of waste (other than special or hazardous wastes) managed according to agency guidelines? _____ Yes _____ No If no, describe:

11. Have there been any known or suspected releases of hazardous substances or petroleum at the site? _____ Yes _____ No If yes, describe:

Have any of the following actions/events been associated with the release(s) described above?

- ___ Hiring of cleanup contractor to remove obviously contaminated materials, including subsoils
- ___ Replacement or major repair of damaged facilities
- ___ Assignment of inhouse maintenance staff to remove obviously contaminated materials, including subsoils

- ☐ Designation as a "significant" release by a state or federal agency
- ☐ Reordering or other replenishment of inventory due to the amount of substance lost
- ☐ Temporary or more long-term monitoring of ground water at or near the site
- ☐ Stop usage of an on-site or nearby water well because of offensive characteristics of the water
- ☐ Coping with fumes from subsurface storm drains or inside basements
- ☐ Signs of substances leaching out of the ground along the base of slopes or at other low points on or adjacent to the site

12. After considering all of the above information, does this site potentially pose a hazard to ground water?
☐ Yes ☐ No If yes, describe:

Inspector: _____

Date inspected: _____

Checklist D-C1 Potential Contaminant Source Short List for Wellhead Protection

If "yes" or "uncertain" is answered to any of the questions below, the appropriate contaminant source worksheets and detailed checklists should be used.

Cross-Cutting Sources (Checklist D-C2)

- ☐ Does the WHPA include natural geologic or hydrogeologic conditions that impair ground-water quality for drinking water? ☐ Yes ☐ No. If yes, evaluate the following options, if this has not already been done:
 - ☐ Look for alternative, higher-quality water supply.
 - ☐ Evaluate effectiveness of existing drinking water treatment system in treating water quality problems.
 - ☐ If there are problems with the existing system, evaluate additional or alternative treatment technologies.
- ☐ Are any active/abandoned wells or boreholes located within the WHPA? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using Checklist D-C2.
- ☐ Are any above- or underground storage tanks in the WHPA? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using Checklist D-C2.
- ☐ Are there any areas of controlled or uncontrolled disposal of wastes in the WHPA? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using Checklist D-C2.

Nonindustrial Sources (Checklist D-C3)

- ☐ Are there any areas within the WHPA used for agricultural, livestock, or forest production? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using the agricultural section of Checklist D-C3.
- ☐ Are there any private homes, apartments, or condominiums within the WHPA? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using the residential section of Checklist D-C3.
- ☐ Are there any nonagricultural, nonresidential areas within the WHPA that receive treatment with fertilizers or pesticides? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using the nonresidential green areas section of Checklist D-C3.
- ☐ Are any areas within the WHPA dedicated for municipal and other public service facilities? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using the municipal/public services section of Checklist D-C3.
- ☐ Are any highways, roads, airports, railroads, pipelines, or associated transportation service and support facilities located within the WHPA? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using the transportation section of Checklist D-C3.

Sources from Commercial, Natural Products Processing/Storage, and Resource Extraction Activities (Checklist D-C4)

- ☐ Are there nonindustrial commercial activities within the WHPA? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using the commercial section of Checklist D-C4.
- ☐ Are there any food, animal, or wood products processing or storage activities located within the WHPA? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using the natural products section of Checklist D-C4.
- ☐ Are there any areas within the WHPA affected by current or past mining, oil and gas production, or other resource extraction activities? ☐ Yes ☐ No ☐ Uncertain If yes or uncertain, conduct inventory using the resource extraction section of Checklist D-C4.

Industrial Sources (Checklist D-C5)

- ___ Are there any chemical processing or manufacturing facilities within the WHPA? ___ Yes ___
No ___ Uncertain If yes or uncertain, conduct inventory using the chemical section of Checklist D-C5.
- ___ Are there any metal manufacturing, fabrication, or finishing facilities within the WHPA? ___ Yes
___ No ___ Uncertain If yes or uncertain, conduct inventory using the metals section of Checklist
D-C5.
- ___ Are there any other manufacturing facilities not included in the two previous categories within the WHPA?
___ Yes ___ No ___ Uncertain If yes or uncertain, conduct inventory using the last section
of Checklist D-C5.

Checklist D-C2 Cross-Cutting Potential Contaminant Sources

Wells and Related Features

Active Abandoned

- | | | |
|-----|-----|---|
| ___ | ___ | Water supply wells |
| ___ | ___ | Monitoring wells |
| ___ | ___ | Sumps and dry wells for drainage |
| ___ | ___ | Geotechnical boreholes |
| ___ | ___ | Oil and gas production wells |
| ___ | ___ | Mineral, oil, and gas exploration boreholes |

For each identified feature, obtain the following information, if possible:

- | | |
|-----|--|
| ___ | Location |
| ___ | Depth |
| ___ | Borehole condition (cased, uncased, sealed, leaky) |
| ___ | Depth to ground water |
| ___ | Ground-water quality |

Storage tanks (see Worksheets D-W8, D-W10, and D-W11)

Above Under
ground ground

- | | | |
|-----|-----|-------------------------------------|
| ___ | ___ | Agricultural |
| ___ | ___ | Residential |
| ___ | ___ | Nonresidential green areas |
| ___ | ___ | Municipal and other public services |
| ___ | ___ | Commercial |
| ___ | ___ | Industrial |
| ___ | ___ | Resource extraction |

For each identified tank, obtain the following information, if possible:

- | | |
|-----|-------------------|
| ___ | Location |
| ___ | Size |
| ___ | Contents |
| ___ | Age and condition |

Waste Disposal Sites

Residential/Municipal Wastewater Treatment

- | | |
|-----|--|
| ___ | Septic tank soil absorption systems |
| ___ | Cesspools |
| ___ | Storage, treatment, and disposal ponds and lagoons |
| ___ | Municipal sewage treatment plant |
| ___ | Municipal sewer lines/lift stations |
| ___ | Wastewater irrigation/artificial ground-water recharge areas |
| ___ | Septage/sewage sludge land spreading areas |

Controlled Waste Disposal/Handling Sites

- | | |
|-----|---|
| ___ | Municipal solid waste landfill (active) |
| ___ | Recycling and waste reduction facility |
| ___ | RCRA Hazardous Waste TSD Facility |
| ___ | Waste surface impoundments/lagoons |
| ___ | Waste injection well |
| ___ | Incinerator: ___ Municipal waste ___ Medical waste ___ Hazardous waste |
| ___ | Demolition/detonation sites |
| ___ | Radioactive waste storage sites |
| ___ | Fire training facilities |
| ___ | Geothermal discharge |

Uncontrolled Waste Disposal Sites

- ___ Accidental spill sites
- ___ Inactive/abandoned hazardous waste site (Superfund)
- ___ Other uncontrolled/ clandestine waste disposal sites, open dumps
- ___ Abandoned mine spoils, mine tailings pile/pond
- ___ Radioactive (uranium mill tailings, laboratory wastes)

For each identified waste disposal, obtain the following information, if possible:

- ___ Location
- ___ Amount and type of waste
- ___ Age
- ___ In-place or planned measures to control contamination

Checklist D-C3 Nonindustrial Potential Contaminant Sources

Residential (Single-Family, Apartments, and Condominiums) — see Worksheet D-W7

- ☐ Common household products
- ☐ Wall and furniture treatments
- ☐ Car maintenance
- ☐ Other mechanical repair and maintenance products
- ☐ Lawns and gardens (EPA/530/SW-90-027i)^a
- ☐ Swimming pools
- ☐ Home-based business (beauty shop, welding, etc. — see Checklist D-C4)

Agricultural (EPA/530/SW-90-027i)^a — see Worksheet D-W8

- ☐ Livestock
 - ☐ Animal feedlots, stables, kennels
 - ☐ Manure spreading areas and storage pits (line/unlined)
 - ☐ Livestock waste disposal areas
 - ☐ Animal burial
- ☐ Chemical storage areas and containers
- ☐ Farm machinery areas
- ☐ Irrigated cropland
- ☐ Irrigation canals
- ☐ Nonirrigated cropland
- ☐ Pasture
- ☐ Orchard/nursery
- ☐ Rangeland
- ☐ Forestland

Other Green Areas (EPA/530/SW-90-027i)^a

Building Grounds

- ☐ Educational/vocational institutions
- ☐ Government offices
- ☐ Other offices
- ☐ Stores
- ☐ Processing/manufacturing facilities
- ☐ Campgrounds
- ☐ Cemeteries
- ☐ Country clubs
- ☐ Golf courses
- ☐ Nurseries
- ☐ Parklands
- ☐ Pest-infested areas (specify type of land use)

Municipal and Other Public Services (see also Checklist D-C2, controlled waste sites)

- ☐ Educational/vocational facilities (EPA/530/SW-90-027i)^a
- ☐ Public swimming pools
- ☐ Sewer/storm water drainage overflows
- ☐ Storm water drains and basins
- ☐ Government service offices
- ☐ Military base/depot

Public Utilities

- ☐ Electric power and steam generation (coal storage areas, ash/FGD disposal areas)
- ☐ Natural gas
- ☐ Telephone/communications

Medical/Care Facilities (EPA/530/SW-90-027m)^a

- ☐ Doctor/dentist offices
- ☐ Hospital
- ☐ Nursing and rest homes
- ☐ Veterinary services

Transportation — see Worksheet D-W9

Airports

- ☐ Active
- ☐ Abandoned air fields

Automobile/Truck (EPA/530/SW-90-027a & 027n)^a

- ☐ Gasoline service stations
- ☐ Truck stops (gasoline plus diesel)
- ☐ Dealers without service departments
- ☐ Dealers with service departments
- ☐ Car rental facilities
- ☐ Government vehicle maintenance facilities
- ☐ Taxicab maintenance facilities
- ☐ School bus maintenance facilities
- ☐ Quick lube shops
- ☐ Repair shops
- ☐ Muffler repair shops
- ☐ Body/paint shops
- ☐ Undercoaters/rust proofing
- ☐ Car washes

Other Point/Areal Sources

- ☐ Boat yards and marinas
- ☐ Road/highway maintenance depots/road salt storage
- ☐ Passenger transit facilities (local and interurban)
- ☐ Railroad yards (EPA/530/SW-90-027k)^a
- ☐ Trucking terminals (EPA/530/SW-90-027k)^a

Linear Sources

- ☐ Highways and roads
- ☐ Railroad tracks
- ☐ Oil and gas pipelines
- ☐ Other industrial pipelines
- ☐ Power line corridors

^a See U.S. EPA (1990a), Table 4.4 for information on how to obtain reference.

Checklist D-C4 Potential Contaminant Sources: Commercial, Natural Products Processing/Storage, and Resource Extraction (See Worksheets D-W10 or D-W11)

Commercial

- ☐ Agricultural chemicals sales/storage (pesticides, herbicides, fertilizers)
- ☐ Barber and beauty shops/salons (EPA/530/SW-90-027q)^a
- ☐ Bowling alleys

Cleaning Services (EPA/530/SW-90-027b)^a

- ☐ Dry cleaners
- ☐ Commercial laundry
- ☐ Laundromats
- ☐ Carpet and upholstery cleaners

Construction Service/Materials (EPA/530/SW-90-027j)^a

- ☐ Plumbing
- ☐ Heating and air conditioning
- ☐ Paper hanging/decorating
- ☐ Drywall and plastering
- ☐ Carpentry
- ☐ Carpet flooring
- ☐ Roofing and sheet metal
- ☐ Wrecking and demolition
- ☐ Hardware/lumber/parts stores
- ☐ Equipment/appliance repair (EPA/530/SW-90-027d)^a
- ☐ Florists
- ☐ Furniture/wood manufacturing repair and finishing shops (EPA/530/SW-90-027c & 027n)^a
- ☐ Funeral services and crematories
- ☐ Heating oil companies
- ☐ Jewelry/metal plating shops (EPA/530/SW-90-027n)^a
- ☐ Leather/leather products (EPA/530/SW-90-027r)^a
- ☐ Lawn and garden care services (EPA/530/SW-90-027i)^a
- ☐ Office buildings and office complexes
- ☐ Paint stores (EPA/530/SW-90-027p)^a
- ☐ Pest extermination services/pesticide application services (EPA/530/SW-90-027i)^a
- ☐ Pharmacies
- ☐ Photography shops, photo processing laboratories
- ☐ Printers, publishers, and allied industries (EPA/530/SW-90-027g & 027p)^a
- ☐ Laboratories (research/testing) (EPA/530/SW-90-027m)^a
- ☐ Scrap, salvage, and junk yards
- ☐ Sports and hobby shops
- ☐ Taxidermists
- ☐ Welders (EPA/530/SW-90-027n)^a

Food/Animal/Timber Products Processing and Storage

- ☐ Canned and preserved fruits and vegetables
- ☐ Canned and preserved seafood processing
- ☐ Soft drink bottlers
- ☐ Grain mills (☐ Grain storage/processing ☐ Animal feed, breakfast cereal, and wheat)
- ☐ Sugar processing (☐ Beet sugar ☐ Cane sugar refining)
- ☐ Dairy products processing (creameries and dairies)
- ☐ Leather products (EPA/530/SW-90-027r)^a
- ☐ Meat products and rendering (slaughterhouses)
- ☐ Poultry and eggs processing
- ☐ Timber products processing
- ☐ Pulp, paper, and paperboard (EPA/530/SW-90-027o)^a
 - ☐ Builders' paper and board mills
 - ☐ Unbleached kraft and semichemical pulp
 - ☐ Pulp, paper, and paperboard
 - ☐ Paper coating and glazing
- ☐ Wood preserving facilities (EPA/530/SW-90-027f)^a

Resource Extraction

- ☐ Abandoned exploration/production wells
 - ☐ Construction materials (sand, gravel)
 - ☐ Coal mining (☐ Active ☐ Inactive)
 - ☐ Uranium mining (☐ Active ☐ Inactive)
 - ☐ Metals mining (☐ Active ☐ Inactive)
 - ☐ Phosphate mining (☐ Active ☐ Inactive)
 - ☐ Natural gas production
 - ☐ Petroleum production/secondary recovery operations
 - ☐ Synthetic fuels (coal gasification, oil shale)
 - ☐ Waste tailings: ☐ Heap leaching ☐ Nonheap leaching
-

^a See U.S. EPA (1990a), Table 4.4 for information on how to obtain reference.

Checklist D-C5 Potential Industrial Contaminant Sources (See Worksheets D-W10 and D-W11)^a

Chemical Processing/Manufacturing

- ___ Explosives (EPA/530/SW-90-027h)^a
- ___ Inorganic chemical manufacturing (EPA/530/SW-90-027h)^a
- ___ Fertilizer manufacturing (EPA/530/SW-90-027p)^a (___ Basic fertilizer chemicals ___ Formulated fertilizer)
- ___ Organic chemical manufacturing and plastics and synthetic fibers (EPA/530/SW-90-027h)^a
- ___ Paint manufacturing (EPA/530/SW-90-027p)^a
- ___ Pesticide formulation (EPA/530/SW-90-027h & 027p)^a
- ___ Petroleum refining/storage
- ___ Pharmaceutical manufacturing (EPA/530/SW-90-027p)^a
- ___ Phosphate manufacturing (___ Phosphorus-derived chemical ___ Other nonfertilizer chemicals)
- ___ Porcelain enameling
- ___ Rubber processing (EPA/530/SW-90-027h)^a (___ Tire and synthetic ___ Fabricated and reclaimed rubber)
- ___ Soaps and detergents (EPA/530/SW-90-027q)^a

Metals Manufacturing/Fabrication/Finishing

- ___ Aluminum manufacturing and forming
 - ___ Aluminum forming
 - ___ Bauxite refining
 - ___ Primary aluminum smelting
 - ___ Secondary aluminum smelting
- ___ Coil coating
- ___ Copper forming
- ___ Electroplating (EPA/530/SW-90-027n)^a
 - ___ Copper, nickel, chrome, and zinc
 - ___ Electroplating pretreatment
- ___ Metal manufacturing and fabrication (EPA/530/SW-90-027n)^a
 - ___ Ferroalloy (smelt and slag processing)
 - ___ Iron and steel manufacturing
 - ___ Metal molding and casting (foundries)
- ___ Metal finishing (EPA/530/SW-90-027n)^a
- ___ Machine and metalworking shops (EPA/530/SW-90-027n)^a
- ___ Nonferrous metals forming

Other Manufacturing

- ___ Asbestos manufacturing
- ___ Asphalt/tar plants
- ___ Battery manufacturing (EPA/530/SW-90-027n)^a
- ___ Cement manufacturing
- ___ Electric/electronic/communications equipment manufacturers (EPA/530/SW-90-027n)^a
- ___ Furniture and fixtures manufacturers (EPA/530/SW-90-027c)^a
- ___ Glass manufacturing
 - ___ Pressed and blown glass
 - ___ Insulation fiberglass
 - ___ Flat glass
- ___ Stone and clay manufacturers
- ___ Textile manufacturing (EPA/530/SW-90-027e)^a

^a See U.S. EPA (1990a), Table 4.4 for information on how to obtain reference.

Checklist D-C6 Risk Categories of Land Uses and Activities Affecting Ground-Water Quality

High Risk (Frequently Prohibited in High-Priority Water Supply Protection Areas)

- ☐ Airport maintenance areas
- ☐ Animal feedlots
- ☐ Appliance/small engine repair shops
- ☐ Asphalt/concrete/coal tar plants
- ☐ Auto repair and body shops^a
- ☐ Boat service, repair, and washing establishments
- ☐ Beauty parlors/hairdressers
- ☐ Business and industrial uses (excluding agriculture) that involve the on-site disposal of process wastes from operations
- ☐ Car washes
- ☐ Chemical/biological laboratory
- ☐ Chemical manufacturing/industrial areas
- ☐ Cleaning service (dry cleaning, laundromat, commercial laundry)^a
- ☐ Disposal of liquid or leachable waste, except for properly designed commercial and residential on-site wastewater disposal systems and normal agricultural operations
- ☐ Electroplaters (metal plating and finishing) and metal fabricators^a
- ☐ Fuel oil distributors
- ☐ Furniture and wood stripping and refinishing^a
- ☐ Gasoline stations
- ☐ Golf courses/parks/nurseries
- ☐ Graveyards
- ☐ Improperly constructed or abandoned wells (perched, confined aquifers)
- ☐ Junkyards and salvage yards^a
- ☐ Landfills and dumps
- ☐ Making the surface of more than 10% of any lot impervious
- ☐ Mining operations
- ☐ Medical services (including dental/vet)
- ☐ Military installations
- ☐ Motels/hotels
- ☐ Municipal sewage treatment facilities with on-site disposal of primary or secondary effluent
- ☐ Oil and gas drilling and production
- ☐ Outdoor storage of road salt, or other deicing materials, the application of road salt, and the dumping of salt-laden snow^a
- ☐ Outdoor storage of pesticides or herbicides
- ☐ Parking areas of over 50 spaces
- ☐ Pesticide/herbicide stores
- ☐ Petroleum product refining and manufacturing
- ☐ Photo processors/printing establishments
- ☐ RCRA hazardous materials TSDs
- ☐ Sand and gravel extraction
- ☐ Trucking or bus terminals
- ☐ Underground storage or transmission of oil, gasoline, or other petroleum products
- ☐ Use of septic system cleaners that contain toxic chemicals (such as methylene chloride and 1,1,1-trichloroethane)
- ☐ Wood preserving and treating^a

Moderate Risk (Frequently Restricted in High-Priority Water Supply Protection Areas)

- ☐ Aboveground storage tanks without secondary containment structures
- ☐ Artificial groundwater recharge facilities
- ☐ Excavation for the removal of earth, sand, gravel, and other soils
- ☐ Drainage from impermeable surfaces without installation and maintenance of oil, grease, and sediment traps
- ☐ Dry wells and unlined storm water drainage channels and impoundments
- ☐ Irrigation in areas with coarse, permeable soils
- ☐ Residential lot size in areas not served by municipal sewers (larger lot sizes reduce the amount of contamination from septic systems and household chemicals)
- ☐ Unlined irrigation canals and tailwater sumps (arid areas)
- ☐ Use of road salt (NaCl)
- ☐ Use of commercial fertilizers, pesticides, and herbicides

^a Highest-risk light industrial uses identified in U.S. EPA (1991).

Sources: Lawrence (1992), Noake (1988), Dean and Wyckoff (1991).

Checklist D-C7 Wellhead Protection Tools

Regulatory Options (Nontechnical)

Zoning Ordinances (Table 11.9)

- ☐ Overlay ground water protection districts (Table 11.8)
- ☐ Land use prohibitions (Table 11.8)
- ☐ Special permitting (Table 11.8)
- ☐ Large-lot zoning (Table 11.8)
- ☐ Transfer of development rights (Table 11.8)
- ☐ Cluster/PUD design (Table 11.8)
- ☐ Growth controls/timing (Table 11.8)

Subdivision and Individual Lot Controls

- ☐ Subdivision ordinances (Table 11.9; see also technical options below)
- ☐ Site plan review (Table 11.9)

Health and Environmental Regulations

- ☐ Prohibit or additional regulation of underground storage tanks (Table 11.8)
- ☐ Other source prohibitions (Table 11.9)
- ☐ Inspection and testing (Table 11.9)
- ☐ Prohibition/regulation of small sewage treatment plants (Table 11.8)
- ☐ Phosphorus buffer zone
- ☐ Septic cleaner ban (Table 11.8)
- ☐ Septic system maintenance/upgrades (Table 11.8)
- ☐ Registration and inspection of businesses using toxic/hazardous materials (Table 11.8)
- ☐ Regulation of household hazardous waste
- ☐ Regulation of agricultural chemicals
- ☐ Regulation of private wells: permits, pump and water quality testing (Table 11.8)

Legislative (State-Level)

- ☐ Establishment of regional WHPAs (Table 11.8)
- ☐ Passage of laws authorizing regulation where regulatory powers are limited

Nonregulatory Options (Nontechnical)

- ☐ Land acquisition by purchase or donation (Tables 11.8 and 11.9)
- ☐ Purchase of development rights (Table 11.9)
- ☐ Taxation deferments for nondevelopment
- ☐ Conservation easements (Table 11.8)
- ☐ Voluntary limits to development (Table 11.8)
- ☐ Land banking/transfer taxes (Table 11.8)
- ☐ Contingency planning (Tables 11.8 and 11.9)
- ☐ Hazardous waste collection program (Table 11.8)
- ☐ Public education (Tables 11.8 and 11.9)
- ☐ Training and demonstration (Table 11.9)
- ☐ Waste reduction (Table 11.9)
- ☐ Water conservation

Technical Regulatory and Nonregulatory Options

General

- ☐ Wellhead protection zones
- ☐ Ground water monitoring (Tables 11.8 and 11.9)
- ☐ Performance standards (Table 11.8)
- ☐ Operating standards (Table 11.9)
- ☐ Design standards (Table 11.9)
- ☐ Best management practices (BMPs) (Table 11.9)
- ☐ Capture zone management

Subdivision Controls

- ☐ Nitrogen/phosphorus loading standards
- ☐ Drainage requirements (Table 11.8)

Non-Point-Source Pollution Controls

- ☐ Agriculture BMPs
- ☐ Construction site BMPs

Appendix D References

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- Lowrence, J.L. 1992. Vulnerability Assessment Criteria: Public Water Supply Protection (Draft). New Mexico Department of the Environment, Santa Fe, NM. [Criteria for giving waivers for constituents to be monitored by drinking water systems]
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APPENDIX E

Aquifer Properties and Contaminant Fate and Transport Problems and Solutions

This appendix provides an integrated set of problems using equations presented in this handbook as an illustration of basic concepts in ground-water flow and contaminant fate and transport. References to the section containing appropriate equations are provided with each question, and answers are provided at the end of the appendix.

E.1 CONTAMINATED SITE CHARACTERISTICS

A 55-gal drum of carbon tetrachloride, a toxic dense nonaqueous phase liquid (DNAPL), has been found tipped over at an industrial facility. The original amount in the drum is not known, so there is some concern whether the spill may have migrated through the aquifer. About 30 ft of unsaturated interbedded sands and clays lie over a sand and gravel aquifer consisting of glacial outwash 40 ft thick. Glacial till 10 ft thick lies over a second aquifer of Cretaceous sandstone. There is an upward hydraulic gradient between the lower and upper aquifers.

Physical characteristics of the two aquifers are as follows (ASTM/USCS grain-size fractions):

Sand and gravel: 10% gravel, 75% sand, 10% silt, 5% clay; bulk density, 1.6 g/cm³

Sandstone: 90% sand, 7% silt, 3% clay; bulk density, 1.7 g/cm³

Well 1, located just upgradient from the spill, has a water level 30 ft below the ground surface, and Well 2, located 2000 ft downgradient, has a water level 35 ft below the ground surface. Well 3, adjacent to Well 1 and cased in the sandstone aquifer, has an elevation 25 ft below the ground surface.

Hint: The following problems will be easier if you draw a stratigraphic cross section with thickness and water elevations.

E.2 GROUNDWATER FLOW

Problem 1. Estimate the hydraulic conductivity of the sand and gravel and sandstone aquifers using the Zhang and Brusseau equation (Section C.2)

Sand and gravel: _____ gpd/ft²

Sandstone: _____ gpd/ft²

Problem 2. Using Darcy's law, calculate the quantity of water that is flowing through the area between Well 1 and Well 2 in the sand and gravel aquifer (Section 2.6.3).

$$Q = KiA = \text{_____} \text{ gpd}$$

Problem 3. Using the modified form of Darcy's law presented in Section 2.6.4, calculate the amount of upward leakage from the lower aquifer into a 10-ft-wide band between the two aquifers. From Figure C.12, it is estimated that the vertical hydraulic conductivity is about 1 gpd/ft².

$$Q_l = (p/m)A\Delta h = \text{_____}$$

Problem 4. What is the porosity of the two aquifers? Hint: Solve Equation 4.7, Section 4.5 for porosity (assume particle density of 2.7 g/cm³).

$$\text{Sand and gravel aquifer } n = \text{_____}$$

$$\text{Sandstone aquifer } n = \text{_____}$$

Problem 5. What is the average interstitial velocity between Well 1 and Well 2 in the sand and gravel aquifer (Section 2.6.5)? (Note: 1 gpd/ft² = 2835 ft/day).

$$\bar{v} = Ki/n = \text{_____} \text{ ft/day}$$

Problem 6. How long will it take the carbon tetrachloride (assuming no retardation) to reach Well 2 once it enters the aquifer (Section 2.6.5)?

$$t = d/v = \text{_____} \text{ days}$$

E.3 CONTAMINANT FATE AND TRANSPORT

Problem 7. Estimate how much the carbon tetrachloride will have dispersed in the sand and gravel aquifer as a result of longitudinal and transverse hydrodynamic dispersion by the time it reaches Well 2 (Section 4.4.2 and C.2). Note: Be careful with units.

$$\text{Longitudinal dispersion } \alpha_l = \text{_____} \text{ ft}$$

$$\text{Transverse horizontal dispersion } \alpha_{th} = \text{_____} \text{ ft}$$

$$\text{Transverse } \alpha_{tv} = \text{_____} \text{ ft}$$

Problem 8. Assuming that carbon tetrachloride has a sorption coefficient of 0.4, what is the retardation factor for transport of carbon tetrachloride in the sand and gravel aquifer (Section 4.5.3)?

$$R_f = [1 + (\rho_b/n)K_d] = \text{_____}$$

Problem 9. The maximum concentration of carbon tetrachloride measured in vertical profile direct-push ground-water samples in the vicinity of the spill is 6500 µg/l. The solubility of carbon tetrachloride in water is 800 mg/l. The EPA guideline for ground-water concentrations indicative

of presence of DNAPL is >1% solubility (Section 5.1.4). Does this concentration indicate presence of DNAPL? ____ Yes ____ No

Problem 10. The possible presence of free-product carbon tetrachloride pooling on clay stringers in the vadose zone was tested by vertical profile soil sampling to a depth of 30 ft in several locations at the site of the spill. The highest total concentration in one of these soil samples was 530 mg/kg. Use the partitioning Equation 4.8 (Section 4.6.1) to estimate soil water concentration. Assume a soil water content of 20%, soil air content of 20%, partition coefficient (K_d) of 0.4, and Henry's constant of 0.94. Using the vadose criterion of estimated soil water content is greater than solubility, is it likely that free-product carbon tetrachloride is present in the vadose zone? ____ Yes ____ No

E.4 ANSWERS TO PROBLEM SET

Problem 1. The Zhang and Brusseau equation requires gravel, sand, silt, and clay percentages. Note that the equation uses percentages rather than decimal fractions.

Sand and gravel:

$$\begin{aligned}\log_{10}k_{(\text{cm/sec})} &= 1.854 - 9.640 \times 10^{-2}(5\%) - 5.936 \times 10^{-1}(10\%)^{0.5} \\ &\quad - 3.478 \times 10^{-2}(75\%) - 4.196 \times 10^{-1}(10\%)^{0.5} = -4.4405 \\ 10^{-4.4405} &= 3.6 \times 10^{-5} \text{ cm/sec} \times 21,200 \text{ (gpd/ft}^2\text{)/(cm/sec)} = 0.77 \text{ gpd/ft}^2\end{aligned}$$

Sandstone:

$$\begin{aligned}\log_{10}k_{(\text{ft/d})} &= 1.854 - 9.640 \times 10^{-2}(3\%) - 5.936 \times 10^{-1}(7\%)^{0.5} \\ &\quad - 3.478 \times 10^{-2}(90\%) - 4.196 \times 10^{-1}(0\%)^{0.5} = -3.1359 \\ 10^{-3.1359} &= 7.3 \times 10^{-4} \text{ cm/sec} \times 21,200 \text{ (gpd/ft}^2\text{)/(cm/sec)} = 15.5 \text{ gpd/ft}^2\end{aligned}$$

Problem 2. Using Equation 2.6 (Darcy's law),

$$Q = KiA = 0.77 \text{ gpd/ft}^2 \times (5 \text{ ft}/2000 \text{ ft}) \times (2000 \text{ ft} \times 40 \text{ ft}) = 154 \text{ gpd}$$

Problem 3. Using Equation 2.7 (modified Darcy's law for upward leakage)

$$Q_1 = (p/m)A\Delta h = (1 \text{ gpd/ft}^2/10 \text{ ft}) \times (10 \text{ ft} \times 2000 \text{ ft}) \times (30 \text{ ft} - 25 \text{ ft}) = 1000 \text{ gpd}$$

Problem 4. Solving Equation 4.7 for porosity and assuming average particle density of 2.70 g/cm³,

$$\text{Sand and gravel aquifer: } n = 1 - \rho_b/\rho_s = 1 - (1.62 \text{ g/cm}^3/2.70 \text{ g/cm}^3) = 0.40$$

$$\text{Sandstone aquifer: } n = 1 - \rho_b/\rho_s = 1 - (1.7 \text{ g/cm}^3/2.70 \text{ g/cm}^3) = 0.37$$

Problem 5. Using Equation 2.8,

$$\bar{v} = Ki/n = 0.77 \text{ gpd/ft}^2 \times (5 \text{ ft}/2000 \text{ ft})/0.40 = 0.004812 \text{ gpd/ft}^2$$

$$0.004812 \text{ gpd/ft}^2 \times 2835 \text{ ft}/(\text{gpd/ft}^2) = 13.64 \text{ ft/day}$$

Problem 6. Using Equation 2.9,

$$t = d/v = 2000 \text{ ft}/13.64 \text{ ft/day} = 146.6 \text{ days}$$

Problem 7. The sand and gravel empirical equation for longitudinal dispersivity uses meters for the input distance; for the appropriate length, conversions need to be made. Since transverse horizontal and vertical dispersion is a ratio, length conversions are not required.

Longitudinal dispersion

$$\alpha_l = 3.4604 \times 10^{-2} (2000 \text{ ft} \times 607.76 \text{ m/ft})^{0.73963} = 114.8 \text{ m} \times 3.28 \text{ ft/m} = 376.6 \text{ ft}$$

Transverse horizontal dispersion

$$\alpha_{th} = 0.28 \alpha_l = 0.28 \times 376.6 \text{ ft} = 105.4 \text{ ft}$$

Transverse vertical

$$\alpha_{tv} = 0.048 \alpha_l = 0.048 \times 376.6 \text{ ft} = 18.1 \text{ ft}$$

Problem 8. Using Equation 4.6,

$$R_f = [1 + (\rho_b/n)K_d] = 1 + (1.62/0.40) \times 0.4 = 2.62$$

Problem 9.

$$\text{No. } 1\% \text{ of } 800 \text{ mg/l} = 8000 \text{ } \mu\text{g/l} > 6500 \text{ } \mu\text{g/l}.$$

Problem 10.

Yes. Equation 4.8 estimates soil water concentration from total soil concentration:

$$C_{sw} = (C_s * bd)/(K_d * bd + S_w + K_h * S_a)$$

$$C_{sw} = (570 \text{ mg/kg} \times 1.62)/(0.4 \times 1.62 + 0.2 + 0.94 \times 0.2) = 890 \text{ mg/l}$$

Carbon tetrachloride solubility = 800 mg/l < 890 mg/l. In other words, some of the total soil concentration includes free-product carbon tetrachloride.

APPENDIX F

Master List of Figures and Tables with Credits

This appendix provides a master list of the figures and tables included in Chapters 1 through 14 in this handbook and includes the following information:

- The source from which the figure or table was obtained. If the figure or table is derived from another source, the original source is also given (e.g., Mercer and Spalding, 1991b, after Portland Cement Association, 1973).
- The page in the handbook where the figure or table is located.
- Full reference citations for figures and tables that are given at the end of the list of tables.

Lists of appendix figures and tables are given at the beginning of the appendices, and reference citations where applicable. Also, the beginning of Appendix D lists and gives the page numbers for worksheets and checklists that are contained in that appendix.

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